Does Size Matter?

Comparing the Alpha-P and the Hyperion for FTIR Paint Analysis

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Abstract

In art and architectural conservation since the 1970s, Infrared Spectroscopy is often used to analyze historic pigments and their media. Fourier Transform Infrared (FTIR) was introduced in the 1980s, followed quickly by the development of the Infrared Microscope. Because the configuration of instruments costs over $100,000 with testing samples priced at hundreds of dollars, it is often cost prohibitive for many conservators, consultants and scientists. Recently, a less expensive and smaller FTIR instrument was introduced. At $15,000 the Brucker Alpha-P presents a much more approachable cost.

In my thesis I wish to compare the results of the pigment and media analysis made with the Alpha-P, located at the institute of Fine Arts to those made on the much larger and more expensive Hyperion FTIR microscope in the Metropolitan Museum's Objects Conservation Laboratory. In addition to investigating the accuracy of the Alpha-P's results, I would also like to discern what the smallest sample size an operator may use before significantly altering the results. There is currently no published information available as to whether this machine performs to the same standards and levels as the larger FTIR microscopy with regard to pigment and media analysis. Because the Alpha-P generally analyses large samples, it may be better applied to architectural pigment testing because of the availability of a more invasive paint sampling than permitted in the world of art conservation. Should this test perform and produce comparable, if not better, results, then the conservation world may find pigment testing more cost effective and easier to execute. In addition to comparing and contrasting the performances of the aforementioned equipment, I would also like to begin to compile library of architectural pigments in media for the Infrared and Ramen Users Group (IRUG) as no such compilation has yet been made available.

Contents

Introduction

> "Mere colour, unspoiled by meaning, and unallied by definite form, can speak to the soul in a thousand different ways."
>
> Oscar Wilde[1]

In his words above, Oscar Wilde describes the power of color over its beholder. When people think about the gift of sight, they often refer to being able to perceive all the colors around them. Color sets a mood, influences decisions and expresses the tastes of individuals. Color is an important part of everyday life. However, its importance is often disregarded in the conservation of finishes in the built environment. This thesis aims make finishes analysis more pervasively used in architectural conservation by comparing two Fourier Transform Infrared instruments.

It could be argued paint analysis in the United States began in 1926 with the restoration of Colonial Williamsburg. Continuing through the end of the 1920s into the 1930s and funded by John D. Rockefeller, the restorations were envisioned to be as authentic as science and research could permit.[2] As construction took place on the structures, paint layers were removed from the interior walls and ornament and studied to determine the 18th century colors of the buildings

[1] Oscar Wilde, "The Critic as Artist, Part II," in *Intentions* (New York: Brentano's, 1905) 199.
[2] Thomas H. Taylor, Jr. and Nicholas A. Pappas, "Colonial Williamsburg Colors: A Changing Spectrum," in *Paint in America: The Colors of Historic Buildings*, Roger W. Moss, ed. (New York: John Wiley & Sons, 1994) 87.
[2] Thomas H. Taylor, Jr. and Nicholas A. Pappas, "Colonial Williamsburg Colors: A Changing Spectrum," 87.

selected by interior designer, Susan Higgenson Nash.[3] Helen Duprey Bullock was also hired to investigate the origin and composition of the paint.[4] By combing through 18th century household inventories, wills, diaries, journals, advertisements and records, Bullock gleaned information that revealed the ingredients of many period paints and finishes.[5] The public was fascinated by the results of her research and they took such notice of the paint that adorned the interiors and exteriors of the buildings that the Williamsburg foundation was persuaded to develop the palette for commercial use under the name of 'Williamsburg Colors'.[6]

Figure 1: Advertisement for Williamsburg Paint Colors, New York Times, 1935

As the United States explored the macro analysis of finishes, England focused on the micro. Joyce Plesters, a scientist at the National Gallery in London, published a groundbreaking

[3] Thomas H. Taylor, Jr. and Nicholas A. Pappas, "Colonial Williamsburg Colors: A Changing Spectrum," 87-89.
[4] Thomas H. Taylor, Jr. and Nicholas A. Pappas, "Colonial Williamsburg Colors: A Changing Spectrum," 88.
[5] Thomas H. Taylor, Jr. and Nicholas A. Pappas, "Colonial Williamsburg Colors: A Changing Spectrum," 88-89.
[6] Thomas H. Taylor, Jr. and Nicholas A. Pappas, "Colonial Williamsburg Colors: A Changing Spectrum," 88.

paper in 1956: C*ross-sections and Chemical Analysis of Paint Samples*.[7] Plesters would develop the practice of paint sample microscopy and micro-chemical pigment analysis which would prove to be the foundation of paint research for the next twenty years.[8] By the time Plesters published her article the idea of examining the layers of paint and finish films was gaining popularity, thanks to her previous research.[9] Unfortunately, much of that research was handicapped by the lack of available laboratory equipment.[10]

Building on Plesters's work and using some of her methodologies, Penelope Hartshorne Batcheler of the National Park Service published the pamphlet, *Paint Color Research and Restoration* in 1963. [11] This was the first widely published article on the subject of finishes research in the United States.[12]

Batcheler wrote her leaflet after working on the restoration of Philadelphia's Independence Hall in the early 1960s.[13] Her approach for determining the various historic finishes layers was by "cratering". Cratering involves creating a small beveled shaped opening through the paint to the substrate.[14] This was the most pervasively used technique in architecture for years. Though the world of finishes conservation would like to declare this technique obsolete, many still find use in its practice.

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[7] Joyce Plesters, "Cross-sections and Chemical Analysis of Paint Samples," *Studies in Conservation*, Vol. 2, No. 3 (April 1956) 110-157.
[8] John Mills, "Obituary: Joyce Plesters," *The Independent*, August 28, 1996, accessed February 20, 2013, http://www.independent.co.uk/news/people/obituary-joyce-plesters-1311884.html#.
[9] Joyce Plesters, "Cross-sections and Chemical Analysis of Paint Samples," 2.
[10] John Mills, "Obituary: Joyce Plesters."
[10]Joyce Plesters, "Cross-sections and Chemical Analysis of Paint Samples," 2.
[11] Penelope Hartshorne Batcheler, "Paint Color Research and Restoration," *American Association for State and Local History Technical Leaflet 15, History News*, Vol.23, No. 10 (Oct. 1968) 1-4.
[12] Patrick Baty, "To Scrape or Not to Scrape?" *Papers and Paints Blog*, Wednesday, January 13, 2010, www.papers-paints.co.uk/scrapes.htm.
[13] Penelope Hartshorne Batcheler, "Paint Color Research and Restoration," 1.
[14] Penelope Hartshorne Batcheler, "Paint Color Research and Restoration," 1-2.

Batcheler made mention of some important techniques for dating and matching the revealed paint. She perceptively writes about paints' visual transformation over time, which was a concept not taken into account in Williamsburg: "Paints may, through time, have visually lost their medium content. To make the pigments optically reflect the light correctly, the surface can be treated with a thin layer of acryloid, i.e. replacing the lost medium."[15] She also was the first to recommend color comparisons with a standardized color system: the Munsell Color Company in Baltimore.[16]

Figure 2: Examples of cratering

During the 1970s paint research expanded dramatically due primarily to advances in spectroscopy. As early as 1800, Sir William Herschel demonstrated the existence of the infrared region in the energy spectrum.[17] But it was not until 1903 that a method of observing the light of

[15] Batcheler, "Paint Color Research and Restoration," 2.

[16] Batcheler, "Paint Color Research and Restoration," 3. Batcheler did not specify whether Acryloid B-72, B-44 or A-21 should be used.

[17] Michele Derrick, Dusan Stulik and James M. Landry, *Scientific Tools for Conservation: Infrared Spectroscopy in Conservation Science* (Los Angeles: The Getty Conservation Institute, 1999) 1.

infrared wavelengths emerged; William W. Coblentz conducted a series of experiments that demonstrated that infrared light could produce spectra of organic and inorganic compounds.[18] The first IR spectrometers were produced just before World War II and refinements in spectrometers led to IR becoming a primary method of analysis by the 1950s.[19]

According to Michele Derrick, "most IR instrumentation used through the 1970s was based on prism or grating monochromators. A major breakthrough in IR technology was the introduction of Fourier transform infrared (FT-IR) spectrometers. These advantages for FT-IR over dispersive instruments translated into practical improvements such as high-speed data collection, increased resolution, lower detection limits, and greater energy throughout."[20] The coupling of the Fourier mathematical analysis with the infrared spectrometer was a boon for art conservation because spectra were gathered more quickly with a concomitant reduction in sample size.

Figure 3: Bruker's first FTIR 1974, bruker.com

Figure 4: Early Spectra Tech IR microscope, ebay.com

[18] Michele Derrick, Dusan Stulik and James M. Landry, *Scientific Tools for Conservation*, 1.
[19] Michele Derrick, Dusan Stulik and James M. Landry, *Scientific Tools for Conservation*, 1.
[20] Michele Derrick, Dusan Stulik and James M. Landry, *Scientific Tools for Conservation*, 1-2.
Jia-Sun Tsang and Roland H. Cunningham, "Some Improvements in the Study of Cross Sections," *Journal of the American Institute for Conservation* Vol. 30, No. 2 (Autumn, 1991) 163-177.

In 1981, a microscope was outfitted to work with the FT-IR spectrometer that allowed the user to target an exact area of the sample for analysis.[21] This instrument became commercially available in 1983, just at the same time the first computer controlled FT-IR became available.[22] Brian Smith writes, "Dave Mattson of Mattson Instruments…pioneered the use of the cube corner inferometer and personal computers for FTIR data acquisition and processing."[23] The computer was further developed in the mid-1980s which allowed for an increase in the power of the processor. This increase led to more accurate data, a smaller sample size and the ability to analyze both organic and inorganic compounds.[24] Soon after, other accessories such as Attenuated Total Reflectance (ATR) and Diffuse Reflectance (DRIFTS) were added, as well as the addition of a diamond cell (figure 6) to the microscope or the spectrometer.[25] More recently a germanium reflected light accessory (figure 7) was added and may be used in place of the diamond cell..

Figure 5: Bruker Hyperion FTIR microscope with the Bruker Vertex

[21] Michele Derrick, Dusan Stulik and James M. Landry, *Scientific Tools for Conservation*, 2.
Brian C. Smith, *Fundamentals of Fourier Transform Infrared Spectroscopy* (Boca Raton: CRC Press, 1996) 6.
[22] Michele Derrick, Dusan Stulik and James M. Landry, *Scientific Tools for Conservation*, 3.
[23] Smith, *Fundamentals of Fourier Transform Infrared Spectroscopy*, 6.
[24] John R. Ferraro. "History of Fourier Transform-Infrared Spectroscopy." Spectroscopy 14, no. 2 (1999): 28-28.
[25] Smith, *Fundamentals of Fourier Transform Infrared Spectroscopy*, 6.

Figure 6: Diamond cell

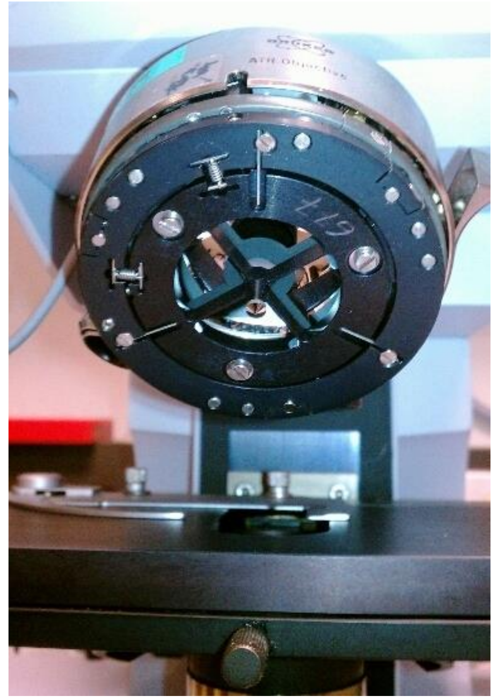


Figure 7: Germanium reflected light accessory on Hyperion microscope

In 2007, Bruker Optics introduced the Alpha-P, a portable Fourier Transform Infrared spectrometer (figures 9 and 10).[26] Unlike a bench FTIR spectrometer-microscope, the Alpha-P measures around 12 inches in depth by 8 and half inches in width, allowing for easy transportation, and may be capable of in situ analysis.[27] A range of attachments is available, which slide into the front of the instrument. These attachments allow for the analysis of solids, liquids and gases.[28] The attachments include a universal sampling module, a diamond cell ATR module, a single reflection ATR module, a DRIFT module and an external reflection module.[29]

[26] "Bruker Optics Expands its FT-IR Product Line with Innovative New Spectrometers," last modified February 27, 2007, http://ir.bruker.com/phoenix.zhtml?c=121496&p=irol-newsArticle&ID=966903&highlight=.
[27] "Alpha FT-IR Spectrometer," last modified 2013, http://www.bruker.com/products/infrared-and-raman-spectroscopy/ft-ir-routine-spectrometers/alpha/overview.html.
[28] "Alpha FT-IR Spectrometer."
[29] "QuickSnap Sampling Accessories," last modified 2013, http://www.bruker.com/products/infrared-and-raman-spectroscopy/ft-ir-routine-spectrometers/alpha/technical-details.html.

Figure 8: Bruker Alpha-P with the external reflection module front end attachment

Figure 9: The attachments are snapped into the front, bruker.com

The focus of this thesis is the comparison of the Alpha-P and the Bruker Hyperion FTIR microscope for pigment and media analysis. Samples of known historic architectural pigments and media were created and analyzed. Many of the paint recipes came from Hezekial Reynold's 1812 book, *Directions for House and Ship Painting*, and others were suggested by paint specialist Dr. Susan Buck.

Methodology

Paint Samples Preparation

Twenty-three different paint samples, using one color per sample, plus two seven-layered samples, were created from recipes outlined in Hezekial Reynold's *Directions for House and Ship Painting*, written in 1812. In addition to using Reynold's book as a source, historic paint specialist Dr. Susan Buck suggested several receipts. All ingredients were as close to the suggested pigments as currently available. All pigments were mulled in pure linseed oil and then brushed onto wood treated with linseed oil. The woods used were ash, maple and pine; the types of substrates one may find in a historic building.

Figure 10: Photograph illustrating the paint making supplies and process

Sample Preparation

To achieve full coverage, between two and four applications of paint were required. Because chalk has a refractive index similar to linseed oil, samples number 1, 2, 3, 5, 11, 15, 16, 17, and 21 required four coats.

Many pigments suggested by Reynolds, such as Spanish brown and rose pink, are no longer available or consist of substances that are of unknown origin or mineralogy. Buck suggested that caput mortuum was the closest to Spanish brown, being a chocolate-purple earth pigment. The rose pink pigment was made from brazilwood, one of the more commonly listed ingredients in the recipes mentioned in Bristow's book on historic house pigments and in Josef Bersch's book on lake pigments.[30] The pigment was made by boiling the wood in water and adding Champagne chalk.[31] The chalk was stirred into the dye until it appeared saturated and then placed in an aluminum pan for drying.[32] The pan was placed in an oven at 150 degrees Fahrenheit and left until all of the liquid had evaporated. The dyed chalk was scraped from the pan, ground and passed through a sieve to remove any remaining wood. After a week in a clear bottle, the exposed pigment became bleached by UV. Thus, this pigment necessitated an amber colored bottle for storage.

[30] Ian Bristow, *Interior House-painting Colours and Technology, 1615-1840* (New Haven: Yale Center for Studies in British Art, 1996) 54, 170.
[31] Josef Bersch, *The Manufacture of Mineral and Lake Pigments*, trans. Arthur C. Wright (New York: D. Van Nostrand Co., 1901) 384-387.
[32] Josef Bersch 384-387.

The Hyperion FTIR Microscope

The Bruker Hyperion FTIR microscope is located at the Metropolitan Museum of Art's Department of Scientific Research, and is attached to a Bruker Vertex 70 Series Spectrometer and a computer. The microscope employs an MCT (mercury-cadmium-telluride) detector cooled with liquid nitrogen. Bruker's OPUS 6.5 is the operating software. Spectra are typically collected in the frequency range 4000 to 600 cm^{-1}, with 4 wavenumber resolution and 64 scans. Attenuated Total Reflectance (ATR) was chosen on the Hyperion as it replicates the capabilities of the Alpha-P's ATR. For each sample a background scan (without the sample) and a single scan are carried out to produce the spectrum.

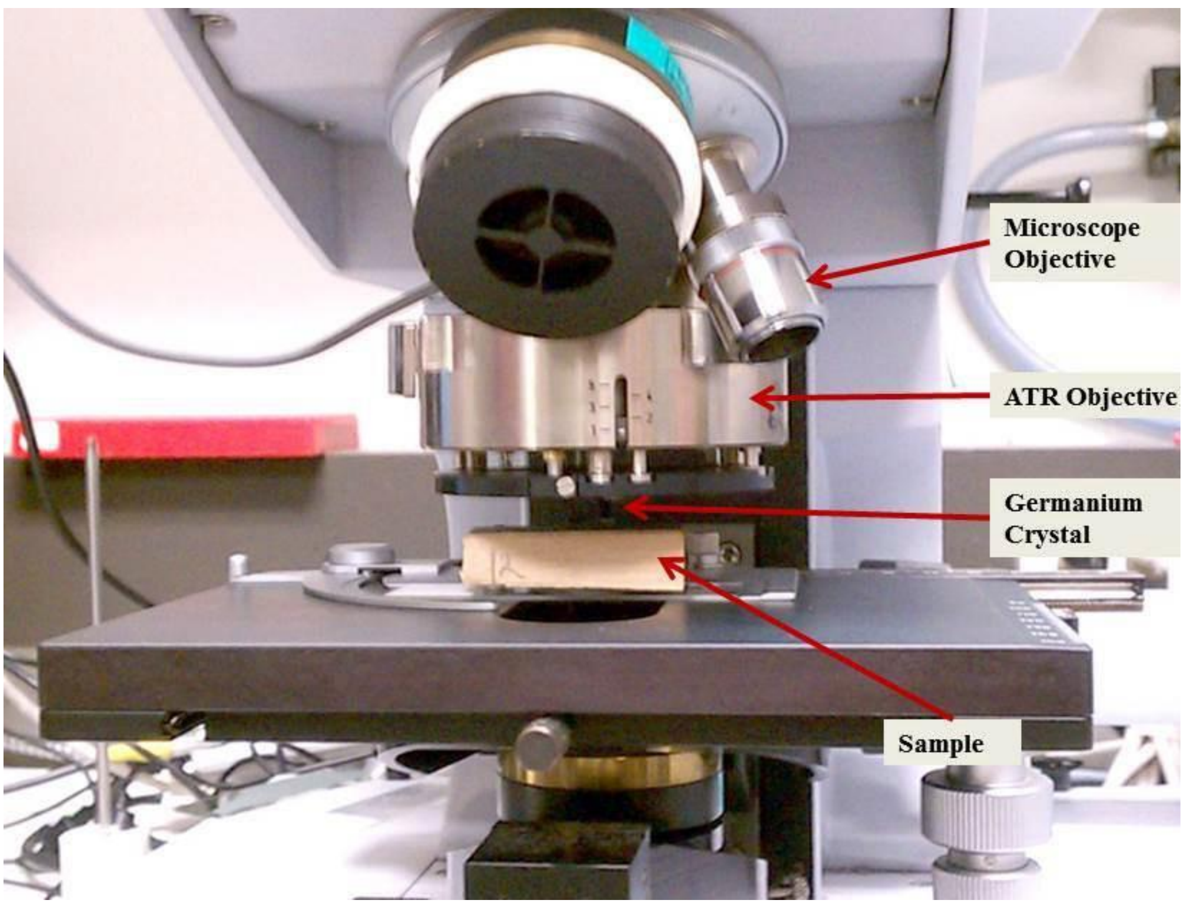


Figure 11: Sample being tested on the Hyperion microscope

The Alpha-P FTIR Spectrometer: ATR Module with the Diamond Cell

Control Sample Test

The Alpha-P also employs OPUS as its operating software with as similar frequency range (4000 to 400 cm^{-1}), the same resolution (4 cm^{-1}) and scans (64). The ATR attachment, known commercially as the "platinum" attachment, consists of a diamond cell embedded in a metal base, over which a sample clamp is assembled. The sample should be level and in complete contact with the diamond by using the clamp to push the sample directly onto the diamond cell. The corner of the sample was used as it provided the best contact; the corner could be tilted into the area where the diamond is located. Because the sample is pressed against the diamond cell, the infrared path is much shorter than with the germanium cell. This means the diamond cell is less likely to pick up as much water vapor as was found with the Hyperion.

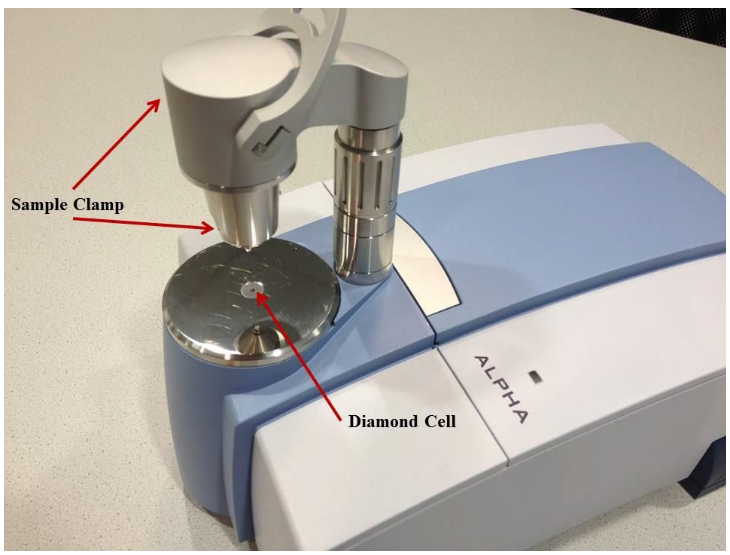


Figure 12: Diagram showing the ATR attachment on the Alpha-P

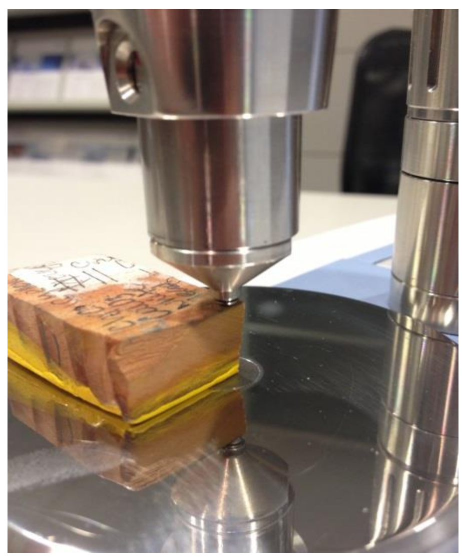


Figure 13: Sample analyzed by the ATR attachment

Powder Analysis

The goal of the second portion of analysis involved determining the smallest amount of powder necessary for an adequate spectrum to be produced. Two single layer control samples, numbers 17 and 22, were chosen based on the strength of their previous Hyperion and Alpha-P ATR spectra. The paint was scraped from the samples' surfaces and pulverized in an agate mortar and pestle.

The full amounts of the powder were applied to the diamond cell and analyzed. For the following test, one-half of the powder was removed and the remainder was analyzed. This powder was continually halved and analyzed until the amounts became too small to halve further. The amounts analyzed for sample 17 were 0.12 mg, 0.06 mg and 0.03 mg; for sample 22 0.7 mg, 0.35 mg, 0.17 mg and 0.085 mg.

Figure 14: 0.7 mg powder from sample 22 on the Alpha-P's diamond cell

Paint Chip Extraction Analysis

The third test on the Alpha-P's ATR was to find the smallest sized paint chip that could be analyzed successfully. A 1 mm sliver was removed through the two paint layers into the substrate of sample 22. The paint sample was placed on the ATR, clamped and analyzed. For each subsequent test, the paint chip was halved until it was the smallest possible size. Those sizes were: 1.0 mm, 0.5 mm, 0.2 mm, 0.1 mm, 0.05 mm, 0.02 mm, 0.01 mm and 0.005 mm.

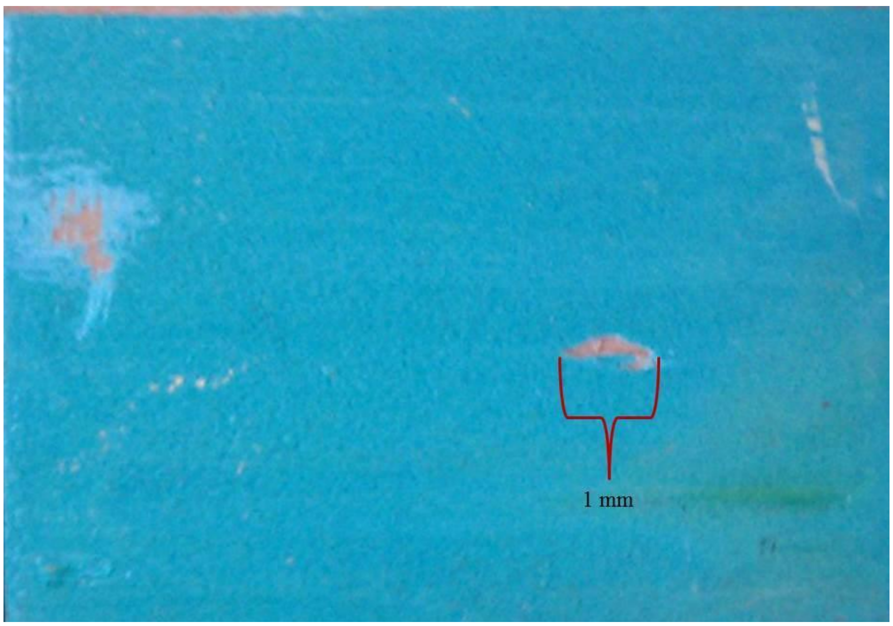


Figure 15: Sample 22 with 1 mm paint sliver removed

The Alpha-P FTIR Spectrometer: DRIFT Module with External Reflection Accessories

Once the first set of samples had been analyzed, the external diffuse reflectance accessory (DRIFTS, figure 16) was used for layered Samples 1 and 2. These samples were created to test the in situ capabilities of the Alpha-P. The paints used were selected from the previous samples, painted on top of one another with a total of seven layers. To speed drying time, the samples were placed in an oven at 300 degrees Celsius in between paint applications.

Figure 16: Front end of the external diffuse reflectance module

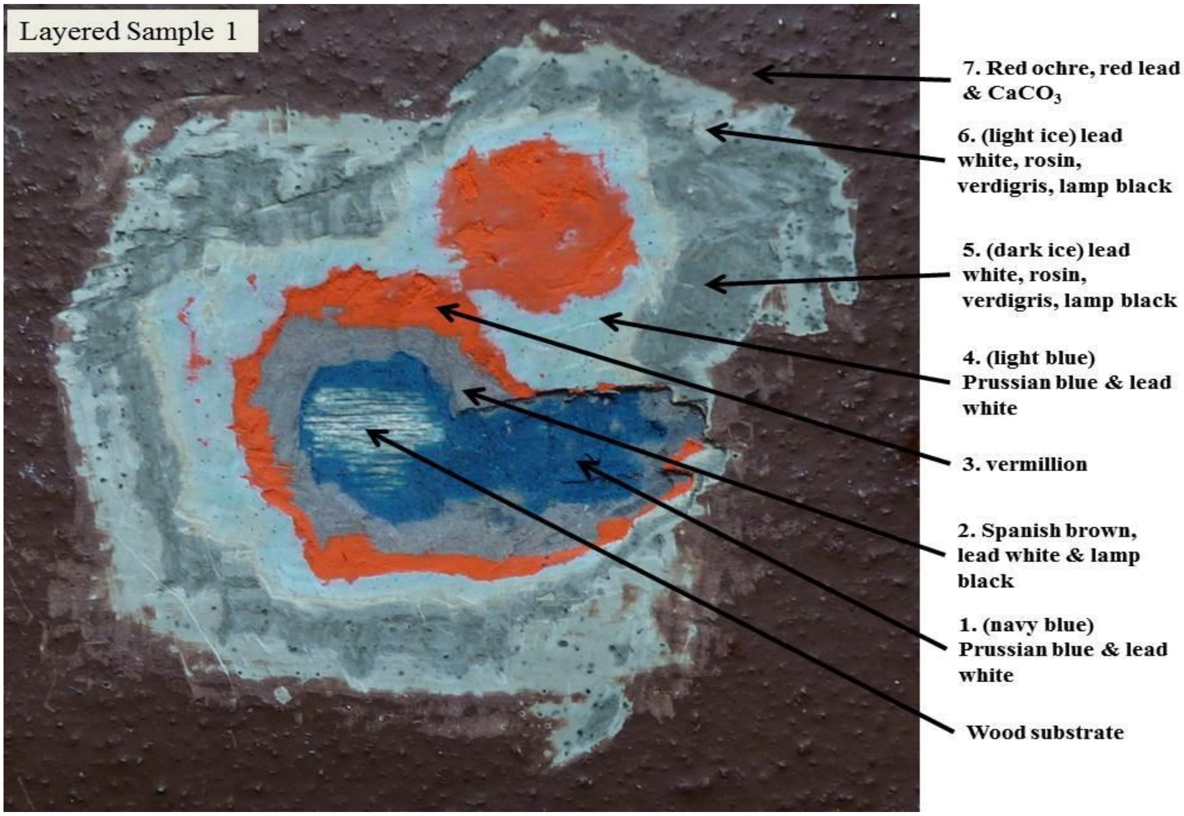


Figure 17: Layered sample 1 identification

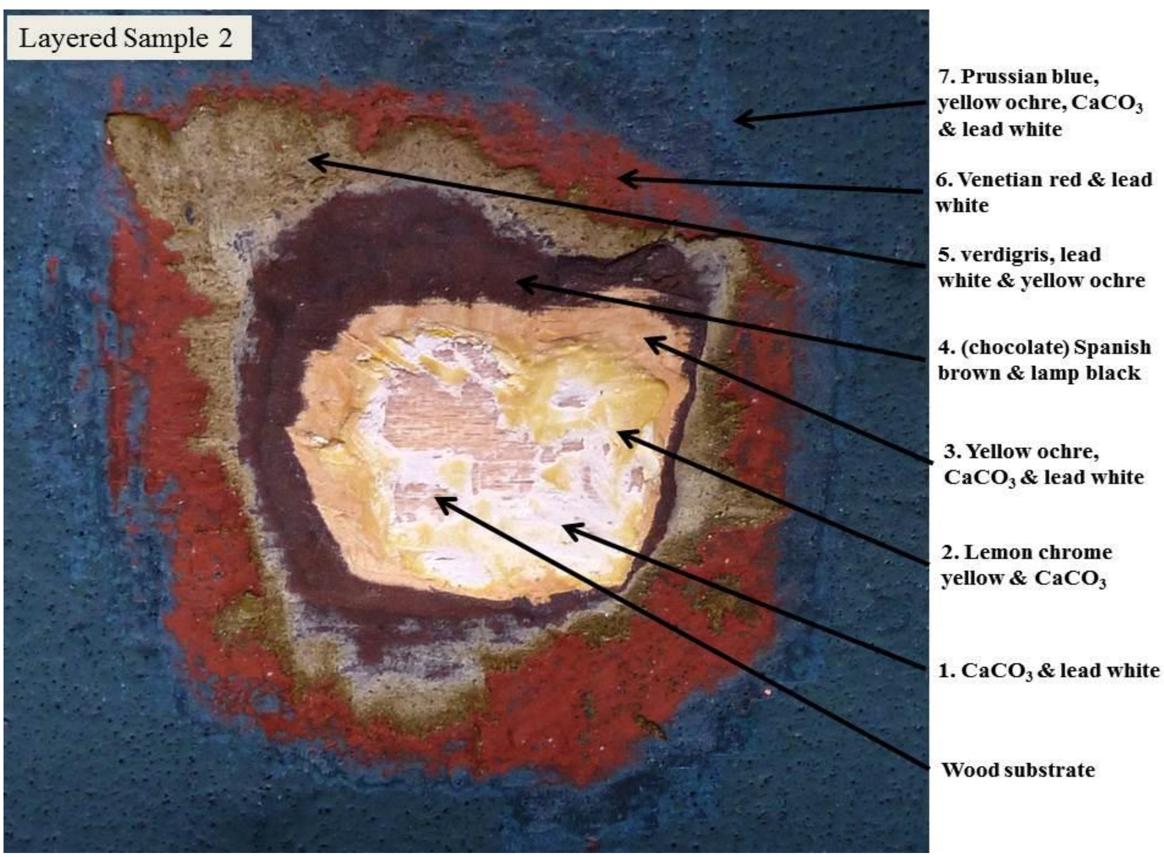


Figure 18: Layered sample 2 identification

The DRIFTS module has several accessories that allow for non-invasive analysis. These accessories, called apertures, have openings that vary depending on the size of the analysis area. The aperture with the smallest hole, measuring 3 mm in diameter, was used for this analysis. In addition, there is an accessory outfitted with a gold plate cover on the interior used for obtaining background spectra.

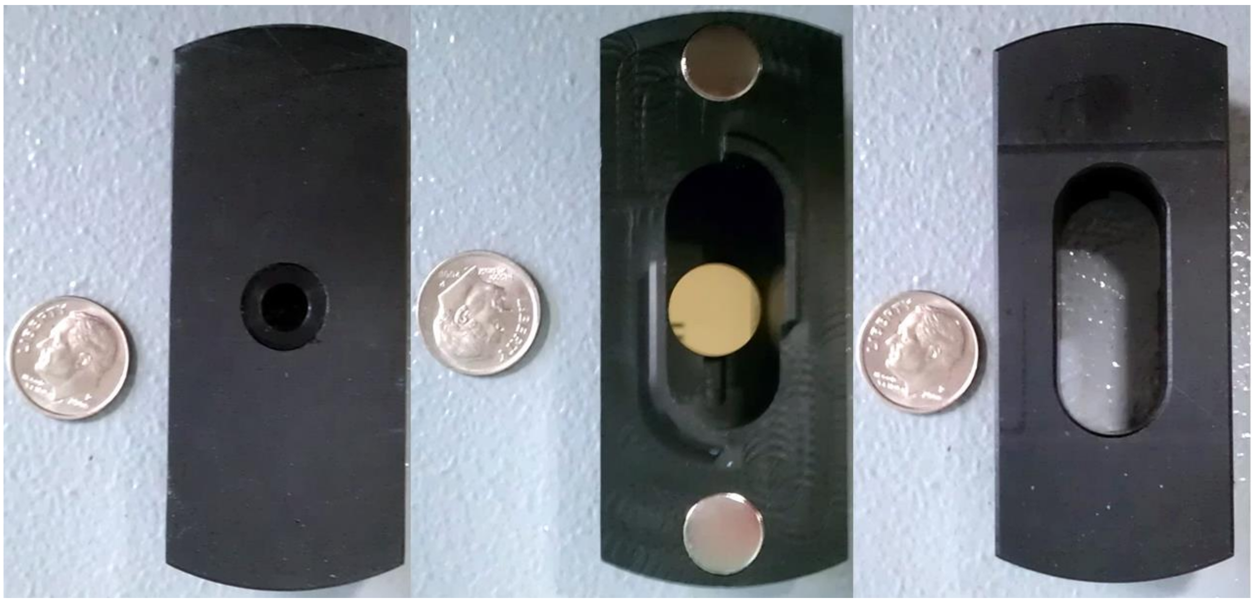


Figure 19: Accessories for the DRIFTS module: 3 mm aperture, background measurement cover and 5 mm aperture

Similar to the previous analyses with the Alpha-P, the DRIFTS attachment did not require as many background measurements as with the Hyperion, thus one was taken every 10 minutes to ensure the accuracy of the spectra. Because the non-invasive measurement accessory places the sample further from the infrared detector, 128 scans were run instead of 64, however the frequency range (4000 to 400 cm^{-1}) and the resolution (4 cm^{-1}) remained the same as in the previous Alpha-P and Hyperion tests. To indicate the area of analysis, the Alpha-P is equipped with an internal camera. For these tests, the samples were manually held in front of the measurement accessory to collect the spectra.

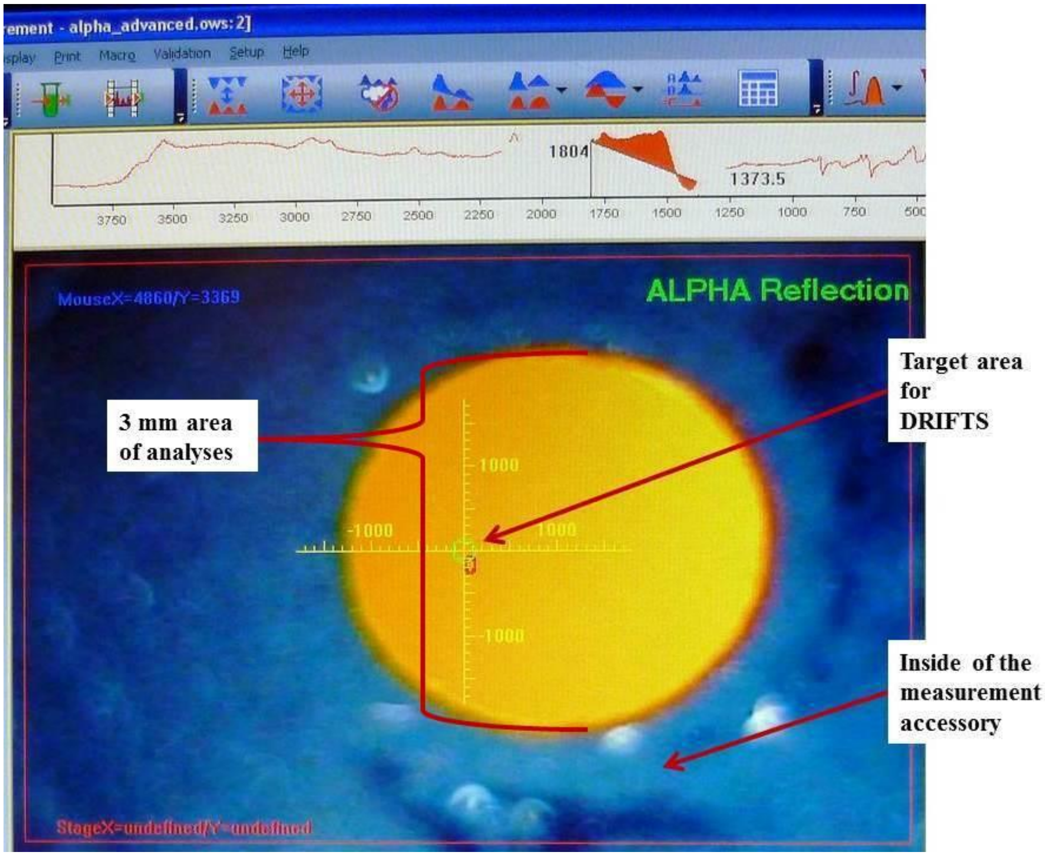


Figure 20: Screenshot of the camera image from the Alpha-P's DRIFTS attachment in OPUS

3. Findings and Discussion

All spectra obtained during the testing on the Alpha-P and the Hyperion are located in the appendix; however a few of those spectra are discussed in this section. It is important to note that the spectra obtained from the three different processes (ATR on the Hyperion and diffuse external reflection and ATR on the Alpha-P) produced three types of spectra. The wavelengths of the spectra depend on the penetration of the device into the sample.[33] Germanium's (Hyperion) penetration is 0.5 microns, the diamond cell's is 2 microns and DRIFTS is 10 microns.[34]

Because of the differences in techniques, it was necessary to convert some of the spectra into like types for comparison. The ATR spectra from the Hyperion were converted from ATR to AB (absorbance) spectra. For the Alpha-P's spectra, the diffuse reflection and the results of the ATR were already in AB. If the ATR spectra were noisy, the Kramers-Kronig transformation could also be used.

Single Color Control Sample Spectra: Carbonate Region

Generally, all spectra obtained on the Alpha-P using the ATR module bore similarity to those acquired by the Hyperion. The area of the Alpha P's spectra that showed the greatest difference was 1500-1000 cm^{-1}. In this region there was a lack of resolution if $CaCO_3$ and/or C (lamp black) were in the paint. One probable explanation is that the diamond cell in the Alpha-P is more susceptible to specular contamination than the germanium crystal.[35] It should be noted that once the bands were less than 1000 cm^{-1}, the Alpha-P's pattern resumed following the Hyperion's.

[33] Tom Tague, email message to author, April 8, 2013.
[34] Tom Tague, email message to author, April 8, 2013.
[35] Tom Tague, email message to author, April 8, 2013.

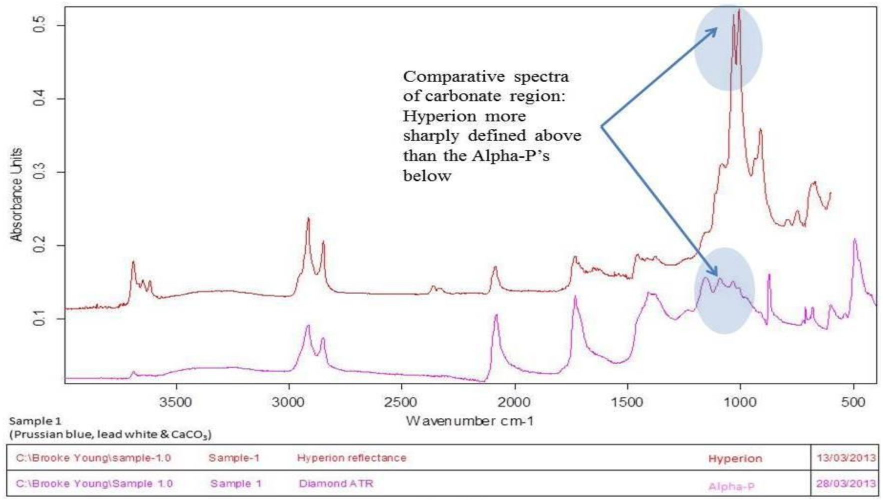


Figure 21: Spectra of Sample 1 showing the differences in absorption in the carbonate region

Single Color Control Sample Spectra: Spectral Shifts

Not only was the definition less clear in the carbonate region on the Alpha-P, but there was also spectral shifting that occurred in comparison to the Hyperion's spectra. The shifting was evident in the carbonate and the carbonyl regions, as seen in the below figure.

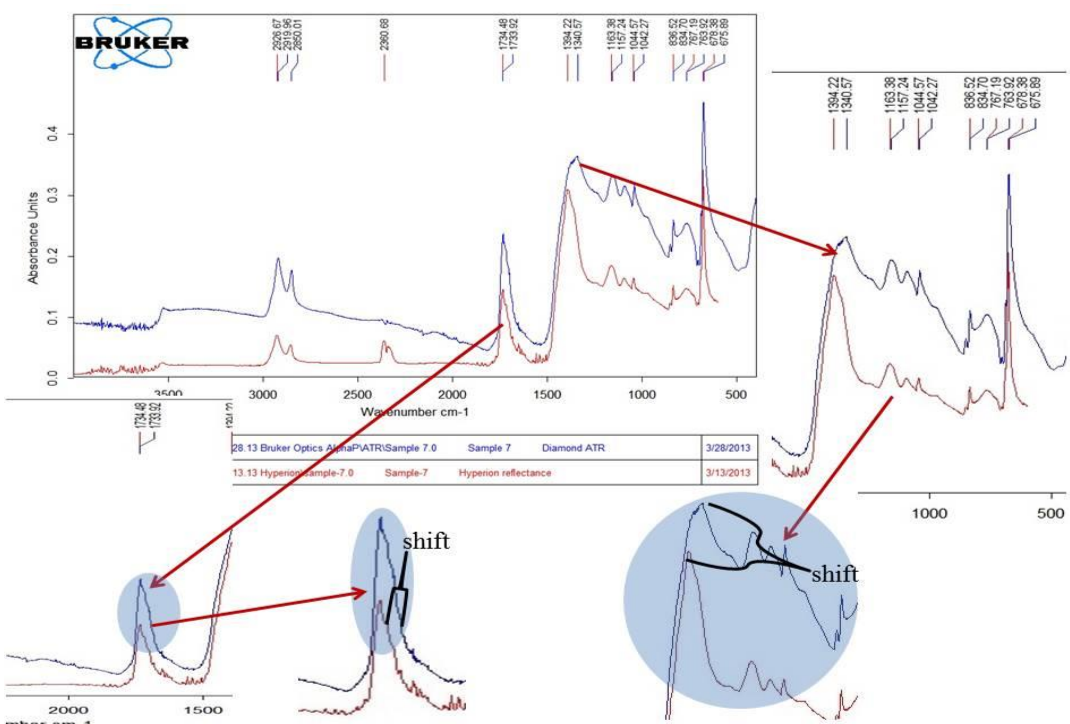


Figure 22: Carbonate and carbonyl regions' shifting in the Alpha-P for Sample 7

This shifting may have created an issue when trying to compare the Alpha-P's spectra to library spectra. The library used was from the Infrared and Ramen Users' Group (IRUG). IRUG is an international collaboration of scientists and conservators who upload and maintain a spectral library of art and architectural materials. When a search was run in the OPUS program using the IRUG library, matches made to the spectra obtained on the Hyperion were successful. However, on the Alpha-P, the library was not always able to make the same matches. For example, a match to lead white was often made, but there were fewer times a successful match was made to the linseed oil medium by itself or other pigments such as Prussian blue or red lead. This example can be seen in the figures 22 and 23 showing the library matches made with sample 6 and sample 3, respectively. It should be noted, however, that it is not uncommon that materials do not make perfect matches.

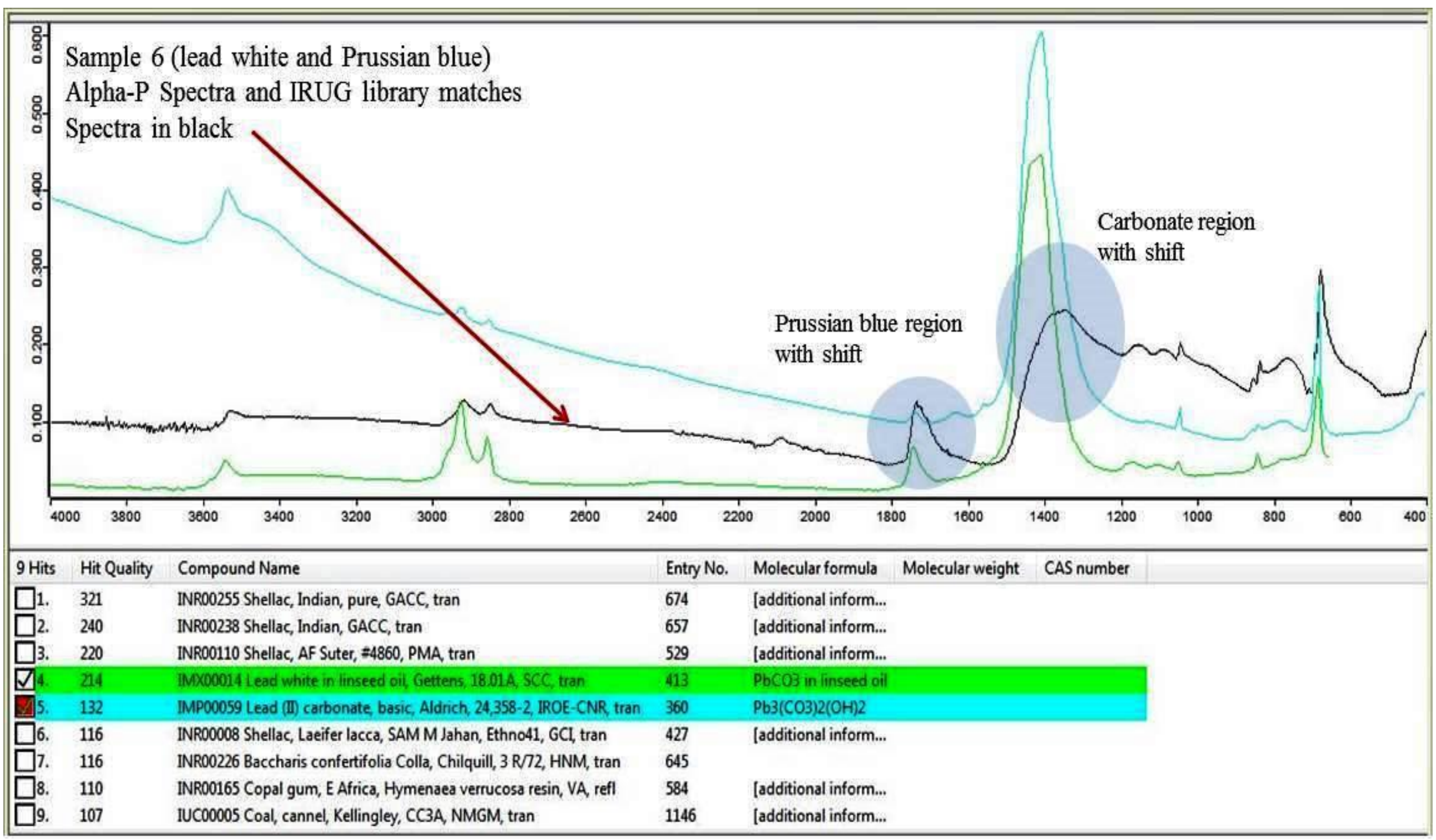
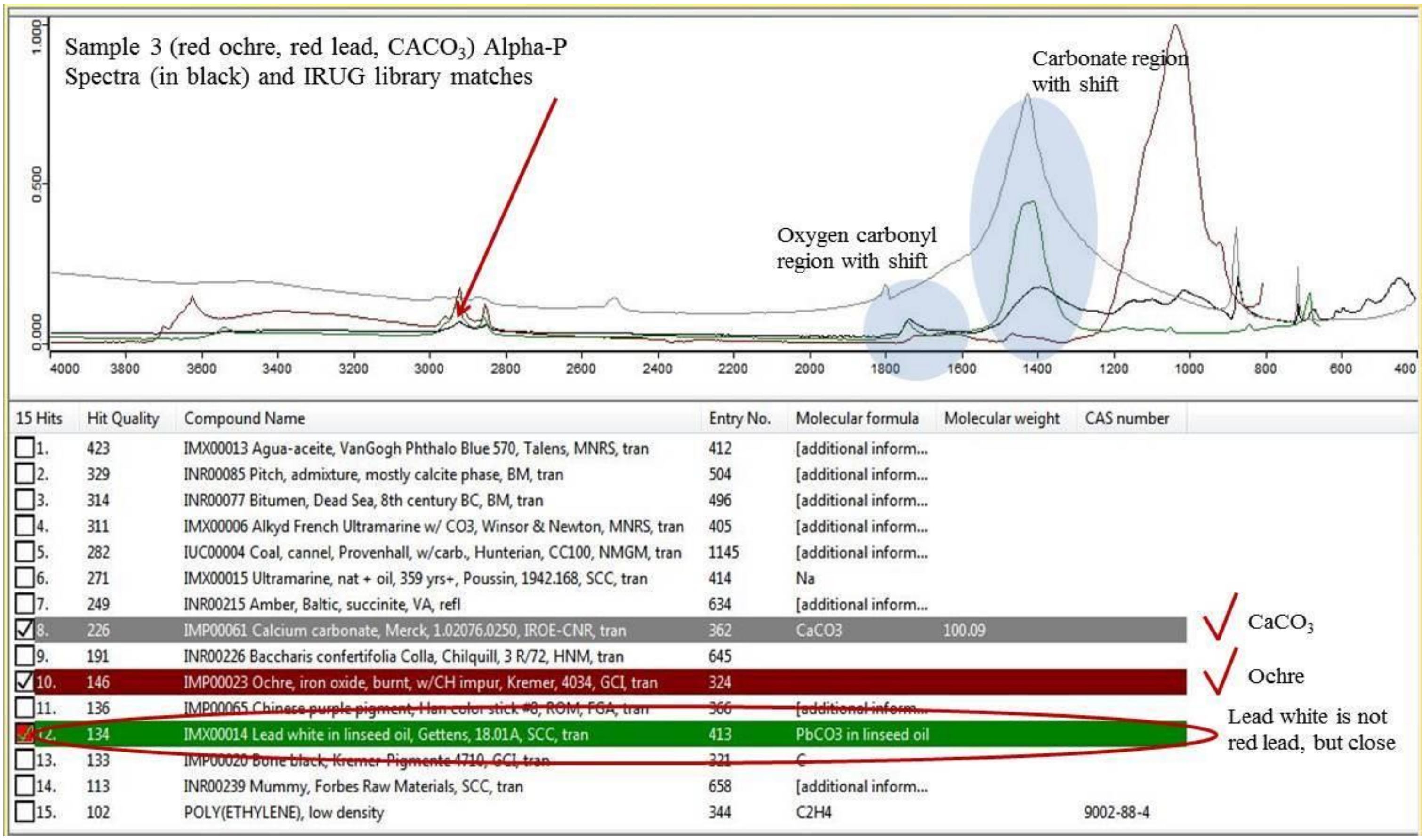


Figure 23: Library matches for sample 6 showing discrepancies in identification



15 Hits	Hit Quality	Compound Name	Entry No.	Molecular formula	Molecular weight	CAS number
1.	423	IMX00013 Agua-aceite, VanGogh Phthalo Blue 570, Talens, MNRS, tran	412	[additional inform...		
2.	329	INR00085 Pitch, admixture, mostly calcite phase, BM, tran	504	[additional inform...		
3.	314	INR00077 Bitumen, Dead Sea, 8th century BC, BM, tran	496	[additional inform...		
4.	311	IMX00006 Alkyd French Ultramarine w/ CO3, Winsor & Newton, MNRS, tran	405	[additional inform...		
5.	282	IUC00004 Coal, cannel, Provenhall, w/carb., Hunterian, CC100, NMGM, tran	1145	[additional inform...		
6.	271	IMX00015 Ultramarine, nat + oil, 359 yrs+, Poussin, 1942.168, SCC, tran	414	Na		
7.	249	INR00215 Amber, Baltic, succinite, VA, refl	634	[additional inform...		
8.	226	IMP00061 Calcium carbonate, Merck, 1.02076.0250, IROE-CNR, tran	362	CaCO3	100.09	
9.	191	INR00226 Baccharis confertifolia Colla, Chilquill, 3 R/72, HNM, tran	645			
10.	146	IMP00023 Ochre, iron oxide, burnt, w/CH impur, Kremer, 4034, GCI, tran	324			
11.	136	IMP00065 Chinese purple pigment, Han color stick #8, ROM, FGA, tran	366	[additional inform...		
12.	134	IMX00014 Lead white in linseed oil, Gettens, 18.01A, SCC, tran	413	PbCO3 in linseed oil		
13.	133	IMP00020 Bone black, Kremer Pigmente 4710, GCI, tran	321	C		
14.	113	INR00239 Mummy, Forbes Raw Materials, SCC, tran	658	[additional inform...		
15.	102	POLY(ETHYLENE), low density	344	C2H4		9002-88-4

Figure 24: Library matches for sample 3 showing discrepancies in identification

Single Color Control Sample Spectra: Powder and Paint Chips on the ATR

While testing for what the smallest sample size could be for powders and paint chips using the Alpha-P's ATR module, it was found that viable spectra could be obtained from samples smaller than typically used in art conservation. Both the smallest powder amounts, 0.085 mg for sample 22 and 0.03 mg for sample 17, produced strong, clear spectra. More definition was observed in the carbonate region of the 0.7 mg sample than in the previous Alpha-P ATR tests, as highlighted in figure 25.

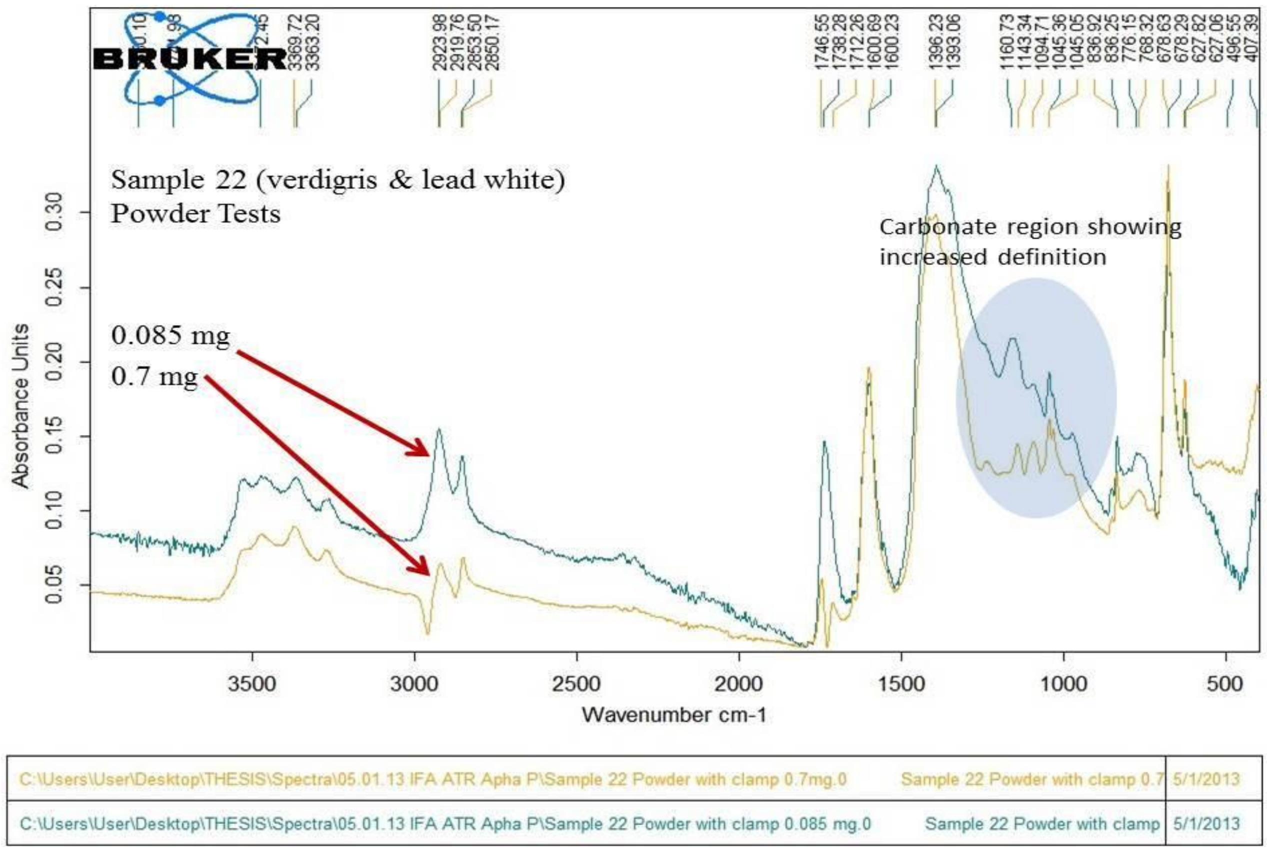


Figure 25: Library matches for sample 6 showing discrepancies in identification

The smallest size analyzed in the paint chip tests was 0.005 mm. The spectra decreased in quality slightly the smaller the size became; however the spectra remained readable each time. The absorption levels in the carbonate region were again less defined, as they were in the first single layer tests. There were also specific increases in the absorption of the 1730 cm^{-1} and the 1030 cm^{-1} band, the carbonyl and carbonate regions respectively. These observations are outlined in blue shading on figure 26.

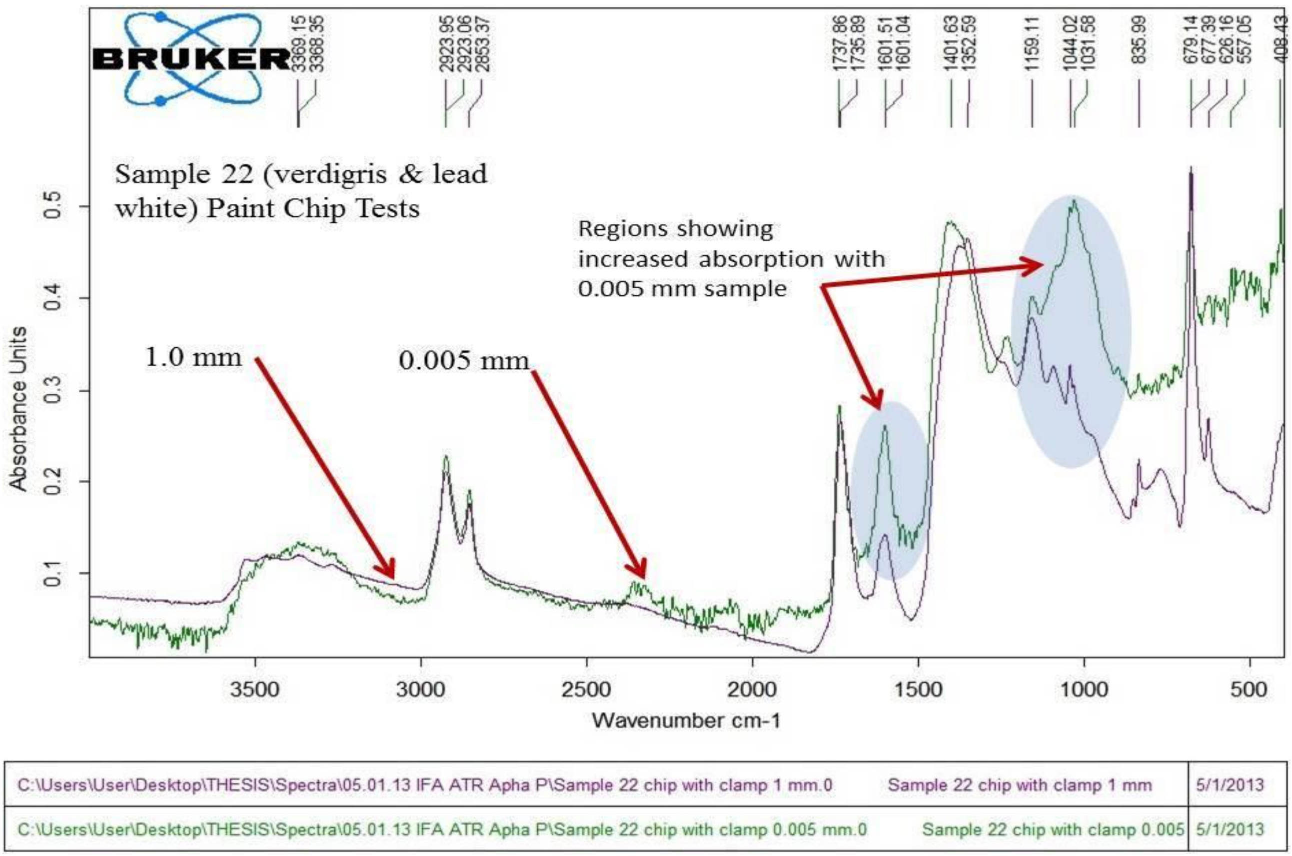


Figure 26: Library matches for sample 6 showing discrepancies in identification

The Alpha-P could easily be used on site with a laptop computer to analyze samples as soon as they are removed from the substrate. Should a surface be too friable for retrieving a sample, a small amount of powder or a paint flake may be removed and analyzed. Either of the aforementioned methods could be done layer by layer, producing instant results in the field.

Layered Control Sample Spectra: In-Situ Analysis

As described in the previous section, layered paint samples were used to test the in-situ capabilities of the Alpha-P. Because the samples were manually held in front of the diffuse reflectance module, there was a concern that the results would be noisy from instability. Results would show that the spectra were readable, but were noisier than the diamond ATR readings on the

Alpha-P (see figure 27 for a comparison). The spectra also had had a few anomalies, such as the Reststrahlen effect, that will be discussed in later sections. Notwithstanding the noise, the spectra could be used to identify the substances in the sample should the operator have a solid knowledge of spectrographic analysis.

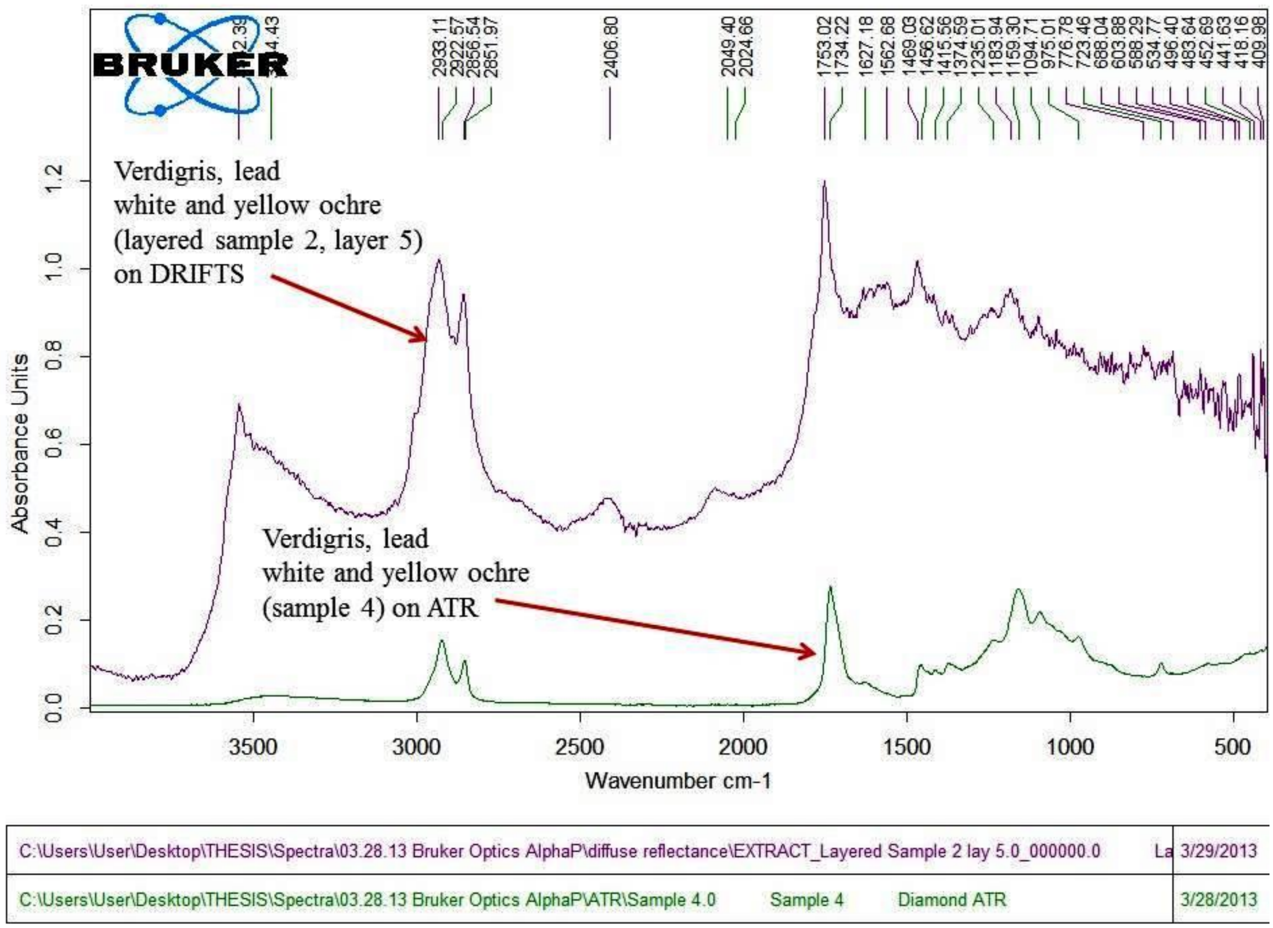


Figure 27: Spectra for verdigris, lead white and yellow ochre on the Alpha-P’s DRIFTS module and ATR module

Layered Control Sample Spectra: the Hydroxyl Region

The region of 3100 to 3500 cm^{-1}, the hydroxyl region, showed noticeable differences in the Alpha-P’s absorption versus in the Hyperion’s. On the Alpha-P’s spectra, there was a sharp peak at or around 3500 cm^{-1} and a noisy descent towards 3100 cm^{-1}. These peaks and troughs appear to be based on the evenness of the sample's surface. For example, the second through the sixth layers' spectra experienced a sharper peak and trough in this region than the first and the seventh layers. The first and seventh layers were the most even on the surface, while the others varied sharply depending on the smoothness of their cratering. Because diffuse reflectance was used on these areas, it is the reflected light that is analyzed. If infrared is not reflected off of an even surface, the spectra will be affected. Therefore, the lack of a level surface may have created the peaks and troughs; as the surface became more uneven by the previous layers of paint or cratering, the peaks become more intense. In addition, there could be contributions from the other paint layers as the IR aperture is 3 mm.

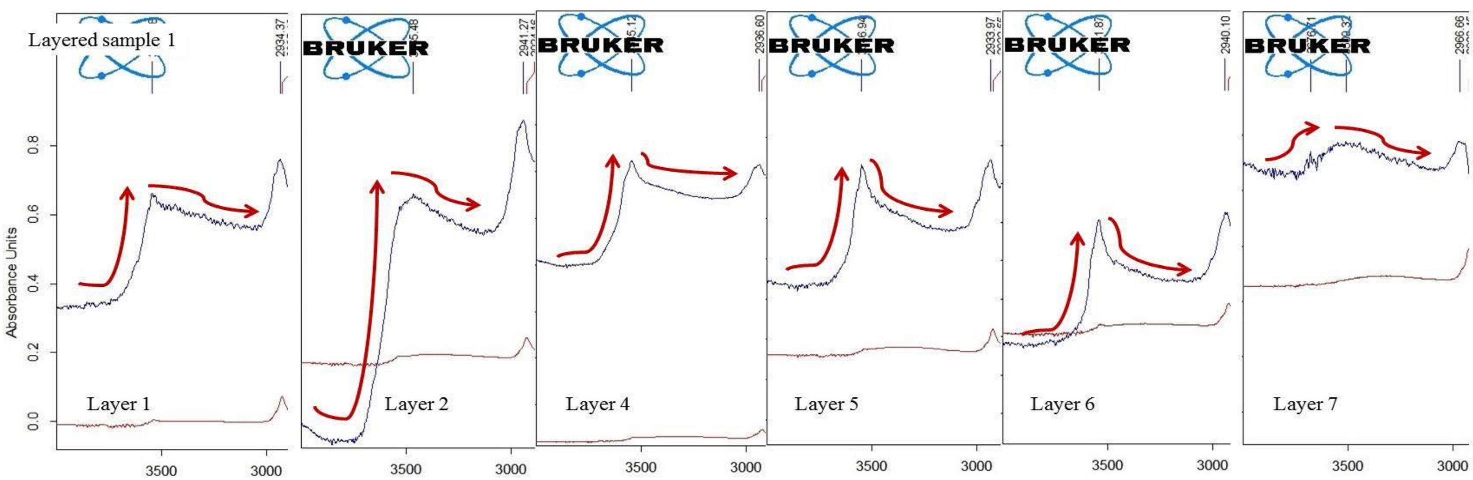


Figure 28: Spectra of Layered Sample 1 showing the decrease in hydroxyl peak size

Layered Control Sample Spectra: the C-H Region 2800 – 2950 cm $^{-1}$

In the Alpha-P's layered samples spectra, there are additional vibrations that appear in the region where carbon-hydrogen bonds absorb infrared (at or around 3000 cm^{-1}). The vibrations appear as a small notch in the absorption peak as is seen in figure 26. This additional vibration may be due to the increase of frequency.[36] When the hybridization of carbon changes from *sp*^{3} to *sp*^{2} to *sp*, the frequency increases.[37] It is this increase in frequency that is being demonstrated by the notches in absorption bands.

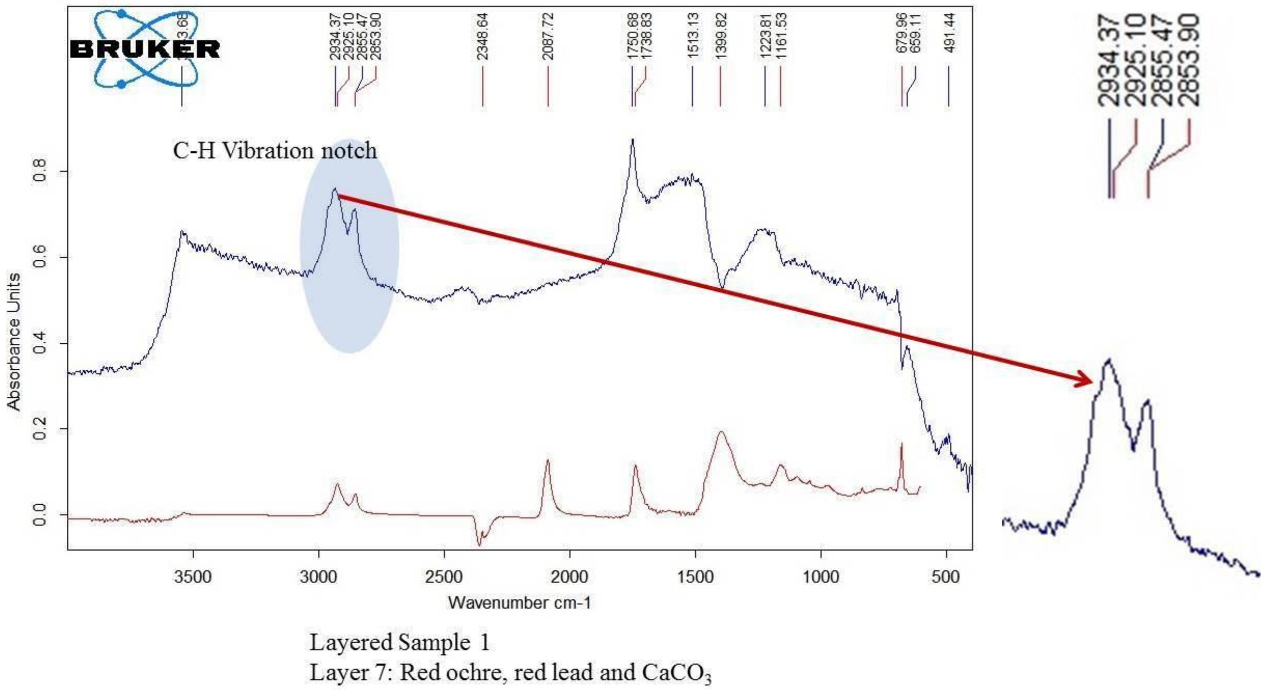


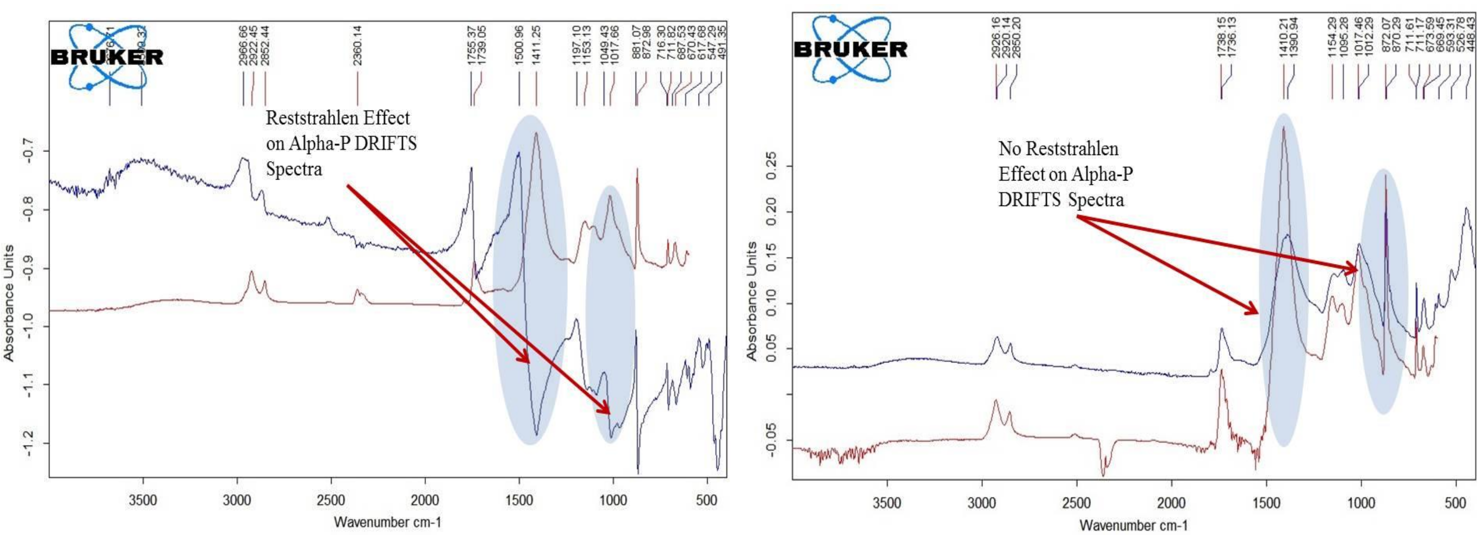
Figure 29: Spectra of Layered Sample 1 showing the decrease in hydroxyl peak size

Layered Control Sample Spectra: Reststrahlen Effect

The Reststrahlen effect is an anomaly that occurs in reflectance spectra that is caused by electromagnetic radiation in a band of energy that is unable to multiply and transmit itself within the sample being analyzed. The band cannot transmit because the sample underwent a change in its refractive index, causing strong or total absorbance by the sample.[38] According to Bronwyn Ormsby et al., "In particular, the specular reflection is governed by Fresnel's law, and depends upon both the

[36] Glenn Gates, instant message to author, May 12, 2013.
[37] Glenn Gates, instant message to author, May 12, 2013.
[38] "Reststrahlen Effect," Last modified 22 March, 2013. http://en.wikipedia.org/wiki/Reststrahlen_effect.

absorption index (*k*) and the refractive index (*n*) and wavenumber. Reflectance spectra of minerals and some organic compounds can be distorted by the inversion of bands showing the $k >> n$ (reststrahlen [sic] effect)."[39] In the spectra, the Reststrahlen effect creates signals that seem negative, which can be confusing in analysis. The negative bands are evident in the left spectra of figure 26. On the right is the spectra of the same paint (red lead, $CaCO_3$ and red ochre) obtained using the ATR. It is evident that there is no Reststrahlen effect as the Alpha-P's bands remain positive. The effect is seen in every Alpha-P spectra obtained from the layered samples.



Layered Sample 1
Layer 7: Red ochre, red lead and $CaCO_3$

Sample 3: Red ochre, red lead and $CaCO_3$

Figure 30: Spectra of layered Sample 1, layer 7 and sample 3 (same paint) showing comparisons of the Reststrahlen effect

[39] Bronwyn Ormsby, Elina Kampasakali, Costanza Miliani, Tom Learner, "An FTIR-Based Exploration of Wet Cleaning Treatments on Artists' Acrylic Emulsion Paint Films" (paper presented at the 8th international conference of the Infrared and Ramen Users' Group (IRUG), Vienna, Austria, 26-29 March 2008), 189.

4. Conclusions

The purpose of this thesis was to examine the capabilities of the Bruker Alpha-P spectrometer in comparison to Bruker's Hyperion microscope. It was important to create several control samples of single and multiple layers using historic paint recipes. It was with these samples that the spectra from the two devices were created and analyzed against one another. It was a vital aspect of this project that both the in-situ and bench properties of the Alpha-P be tested. To do so, spectra were run on both the ATR diamond cell module (bench) and the DRIFTS module (in-situ).

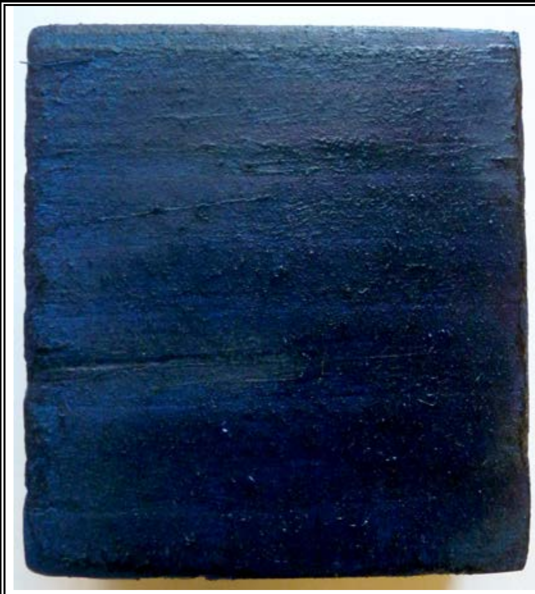
Once the spectra were compared, it was evident that the Alpha-P could produce viable spectra from both modules. All spectra show that the Alpha-P may be taken out in the field to use directly on cratered or revealed surfaces by use of a tripod. The Alpha-P is also capable of analyzing samples as soon as they are removed, either as a powder or a paint chip. Testing proves that sample amounts as small as 0.03 mg and 0.005mm can produce noiseless spectra.

The differences in the capabilities of the Hyperion and the Alpha-P were evident in the Alpha-P's spectra. There were discrepancies in the carbonate region that made the spectra difficult to analyze. The shifting in the carbonyl region prohibited a successful use of matching with the IRUG library in the OPUS software. In addition, the in-situ tests showed that the results were affected in the hydroxyl region when the surface being analyzed was uneven. The most striking difference between the Hyperion and Alpha-P's spectra was the Reststrahlen effect that was prevalent in the 1600 to 700 cm^{-1} region, however this anomaly is not singular to the Alpha-P's diffuse reflectance; it has been seen on other devices as well.

Going forward, an effort must be made to create a spectral library for the Alpha-P. It would be useful to create a library so that the lack of definition in the carbonate region and the effect may be taken into account. It would also be helpful to create a library of reflectance spectra in order to speak towards the Reststrahlen effect. Another opportunity is for Bruker to create a calculation in the OPUS software that could correct one or all of the aforementioned discrepancies. Most ideal would be a calculation that could eradicate the shift and define the carbonate region so that extant libraries could be used. Should none of the above be possible, an HCl wash applied to any sample high in carbonate content could help to define that region in the spectra.

There are many questions that remain in regards to the Alpha-P's efficacy. Can the spectra form both the attenuated reflectance and diffuse reflectance be tailored in a way to become readable to a scientist or conservator without spectrographic training? Can the Alpha-P be tuned so that the carbonate areas can become more defined when using the diamond cell? Would using an HCl wash on carbonate samples prior to analysis help the lack of definition? Is there any way to diminish the Reststrahlen effect? This thesis resolves only a few of the surface issues with the Alpha-P's uses. However, testing has shown it to be an instrument capable of a large "spectrum" of possibilities with the flexibility of both bench and in-situ use.

Appendix 1: Single Color Control Samples Information & Spectra



Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 1

PIGMENTS:

Prussian Blue, Lead White, $CaCO_3$

CHEMICAL COMPOUNDS:

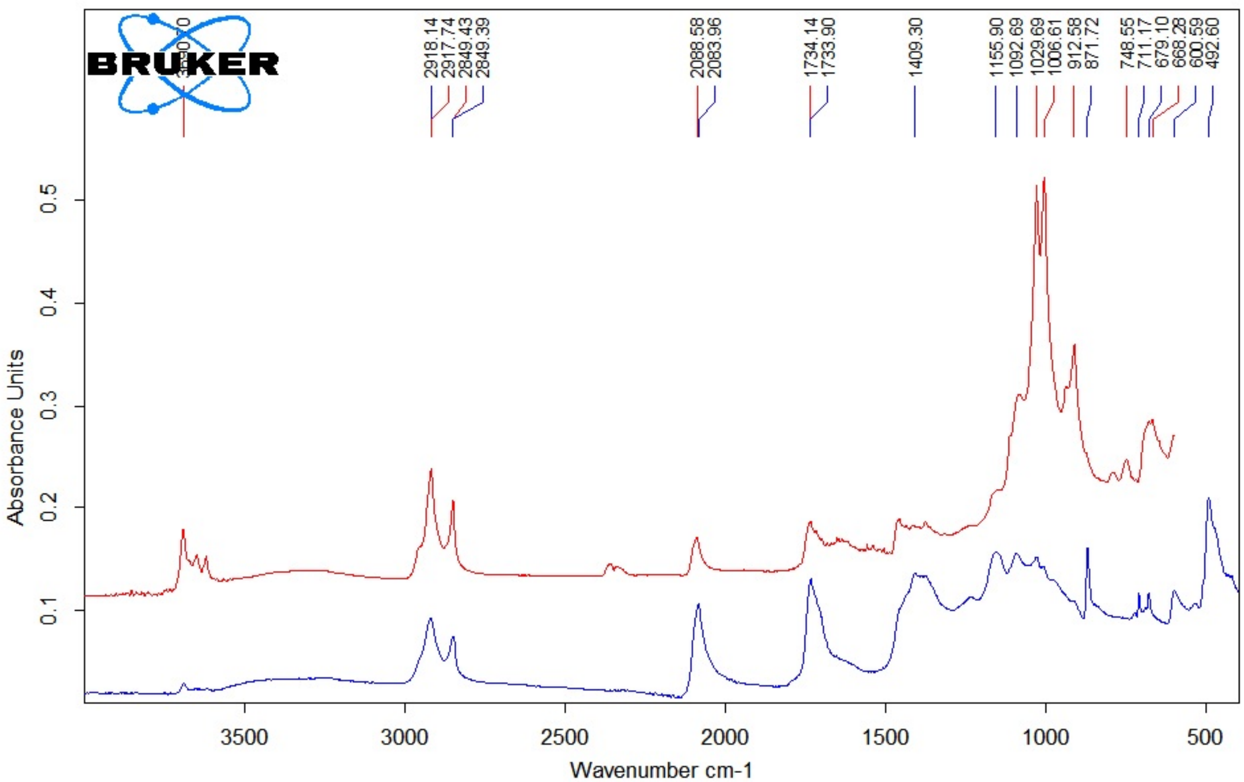
$Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$

$2PbCO_3 \cdot Pb(OH)_2$

$CaCO_3$

RECIPE ORIGIN: Susan Buck

Alpha-P & Hyperion Spectrum



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Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 2

PIGMENTS:

Prussian Blue, Yellow Ochre, Lead White, $CaCO_3$

CHEMICAL COMPOUNDS:

$Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$

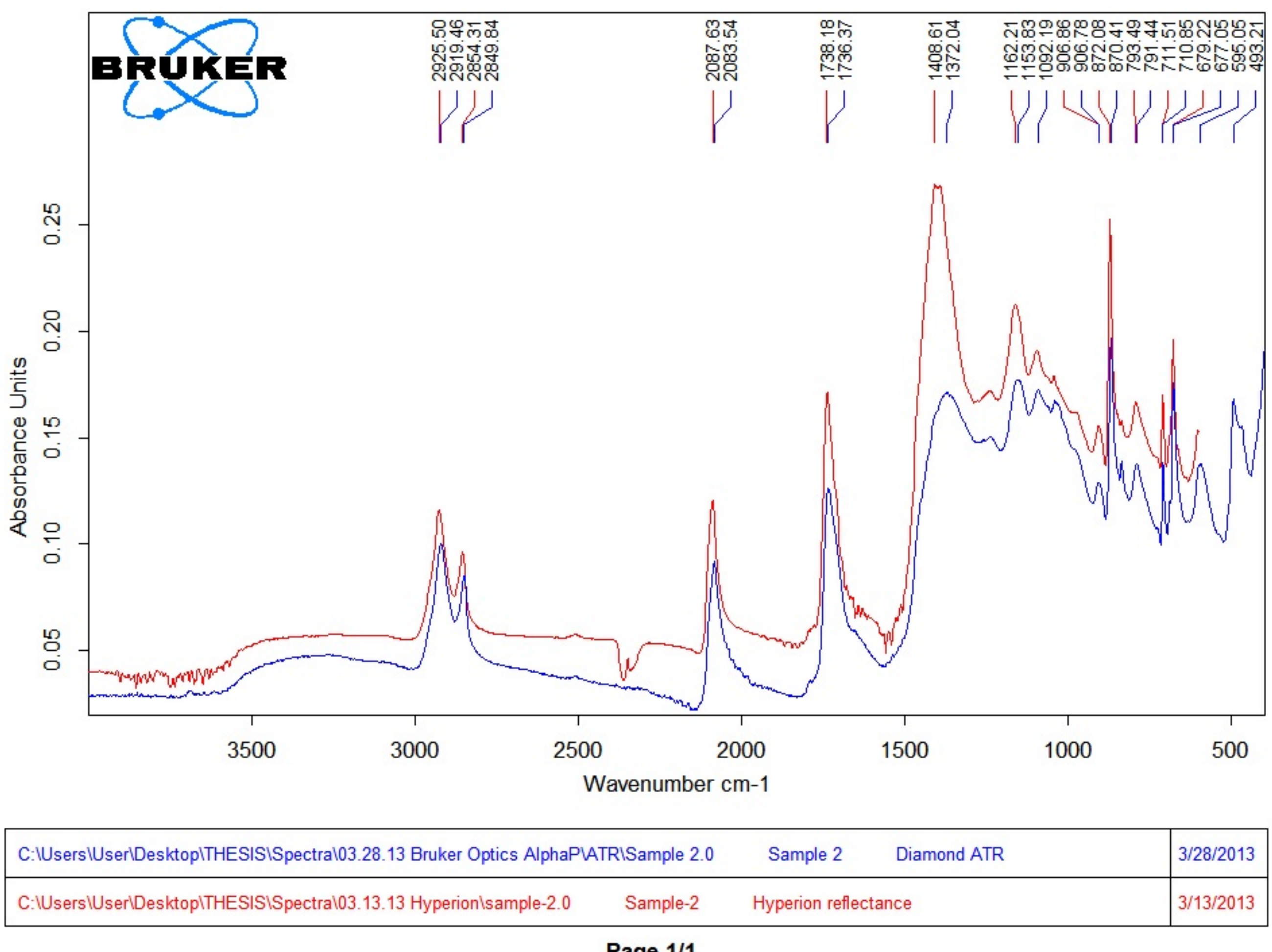
Fe_2O_3

$2PbCO_3 \cdot Pb(OH)_2$

$CaCO_3$

RECIPE ORIGIN: Susan Buck

Alpha-P & Hyperion Spectrum



Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 3

PIGMENTS:

Red Ochre, small amount Red Lead, $CaCO_3$

CHEMICAL COMPOUNDS:

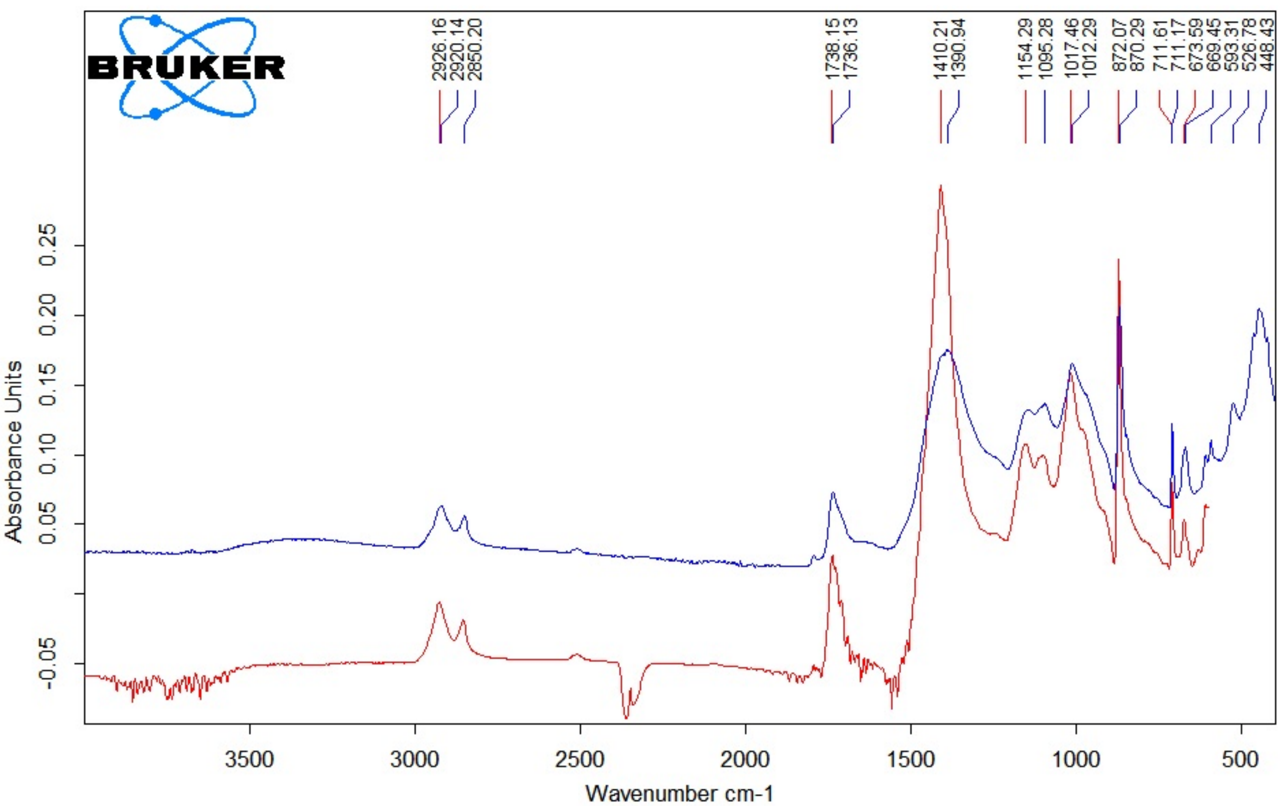
Fe_2O_3

Pb_3O_4

$CaCO_3$

RECIPE ORIGIN: Susan Buck

Alpha-P & Hyperion Spectrum



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Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 4

PIGMENTS:

Verdigris, Yellow Ochre, small amount Lead White with Black Smalt blown on top

CHEMICAL COMPOUNDS:

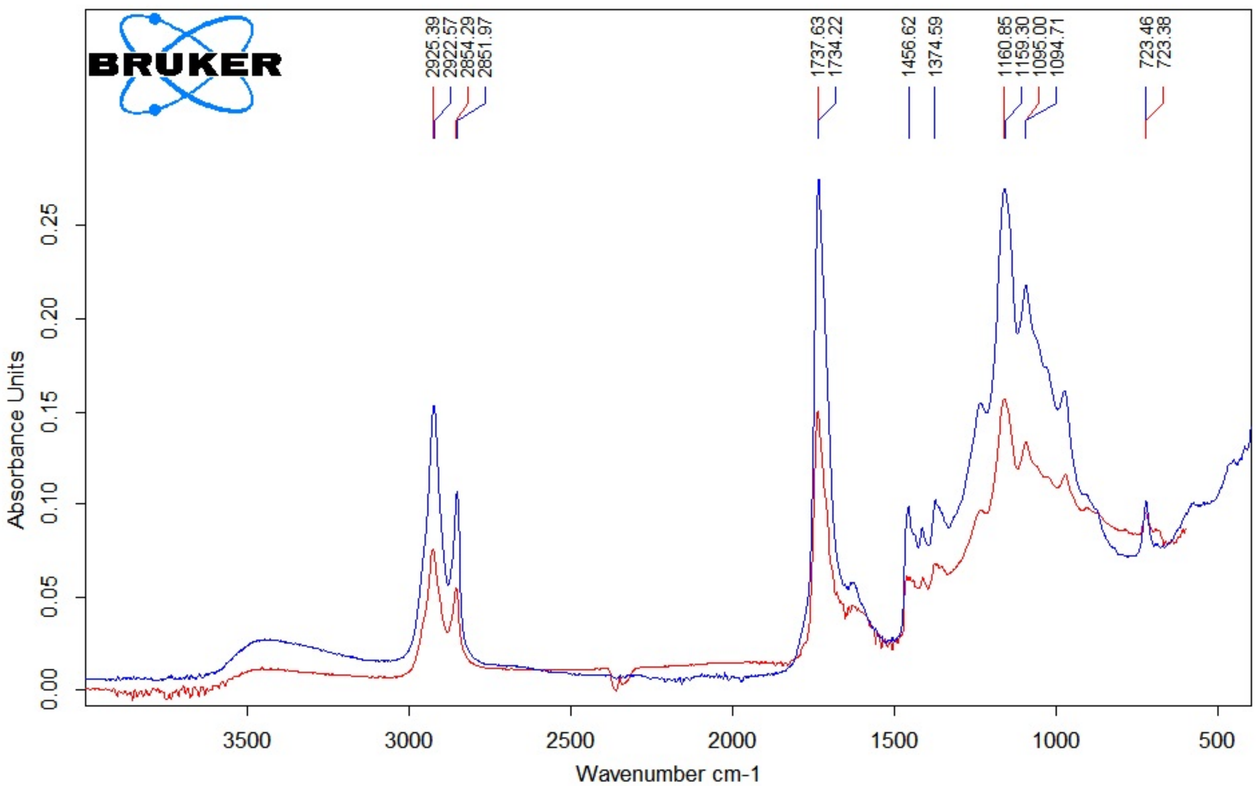
$Cu(OH)_2 \cdot (CH_3COO)_2 \cdot 5\ H_2O$

$FeO(OH))$; $2PbCO_3 \cdot Pb(OH)_2$

SiO_2(65%) + K_20 (15%) + Al_2O_3 (5%) + CoO (10%)

RECIPE ORIGIN: Susan Buck

Alpha-P & Hyperion Spectrum



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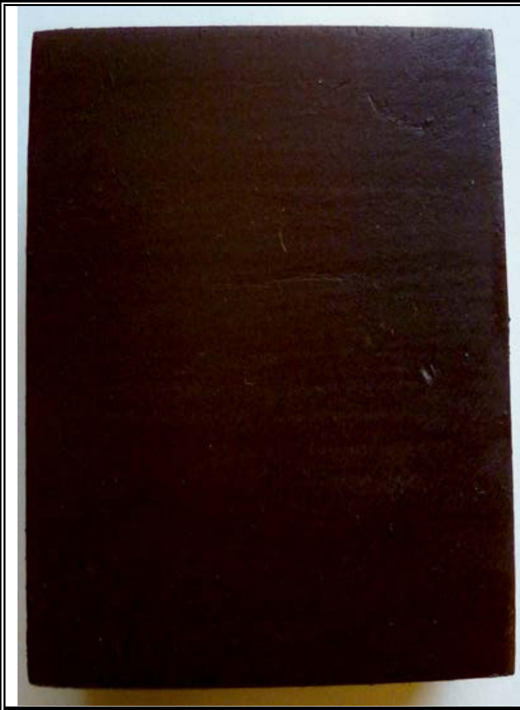


Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 5

PIGMENTS:

Red Ochre, Lamp Black, small amount Red Lead, $CaCO_3$

CHEMICAL COMPOUNDS:

Fe_2O_3;

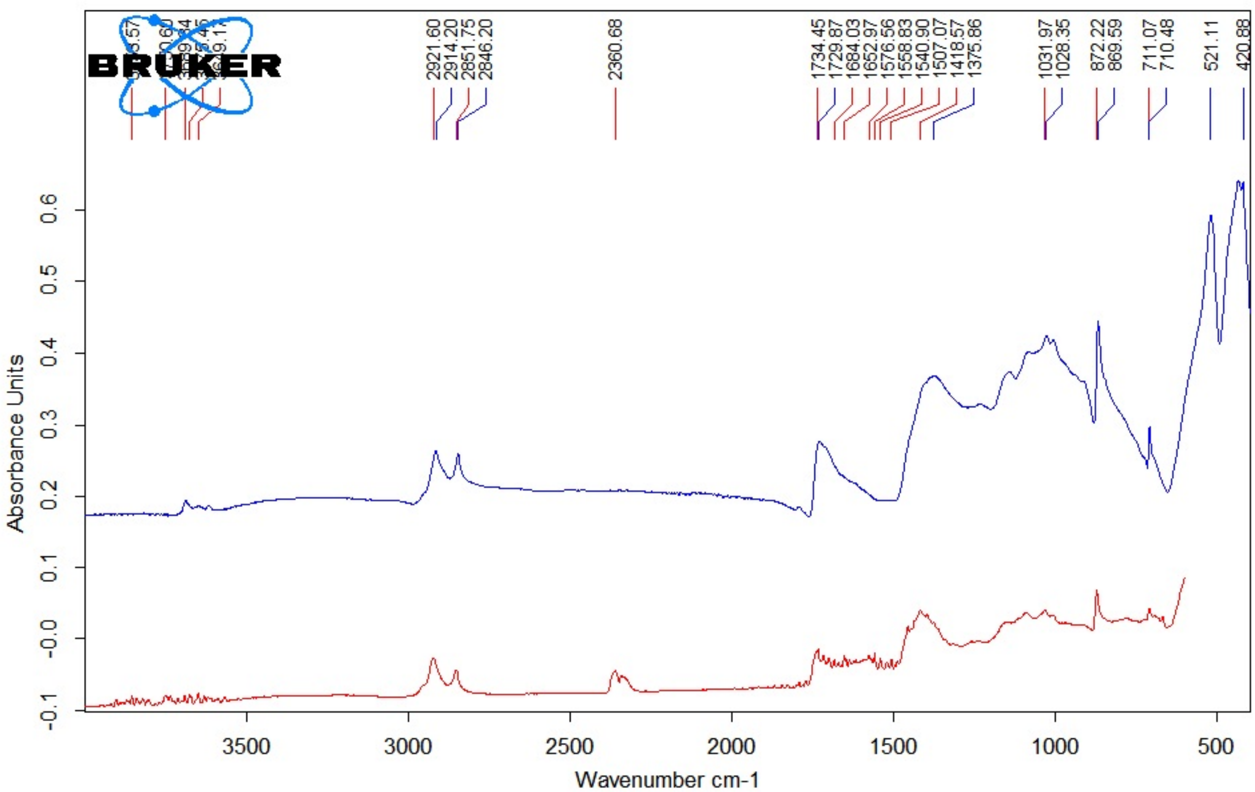
C;

Pb_3O_4;

$CaCO_3$

RECIPE ORIGIN: Susan Buck

Alpha-P & Hyperion Spectrum



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Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 6, Prussian Blue Color

PIGMENTS:

Prussian Blue, Lead White

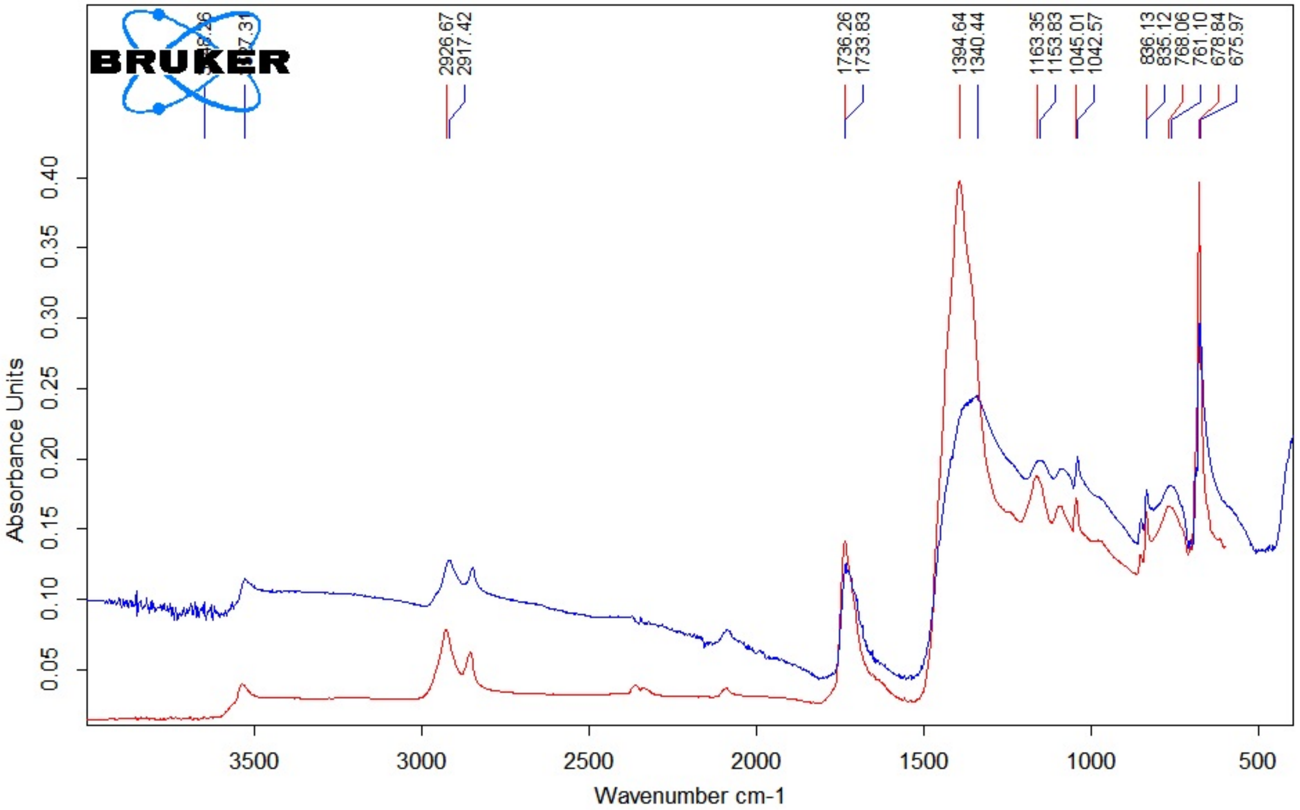
CHEMICAL COMPOUNDS:

$Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$

$2PbCO_3 \cdot Pb(OH)_2$

RECIPE ORIGIN: Hezekial Reynolds

Alpha-P & Hyperion Spectrum



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Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 7, Sky Blue

PIGMENTS:

Prussian Blue, Lead White

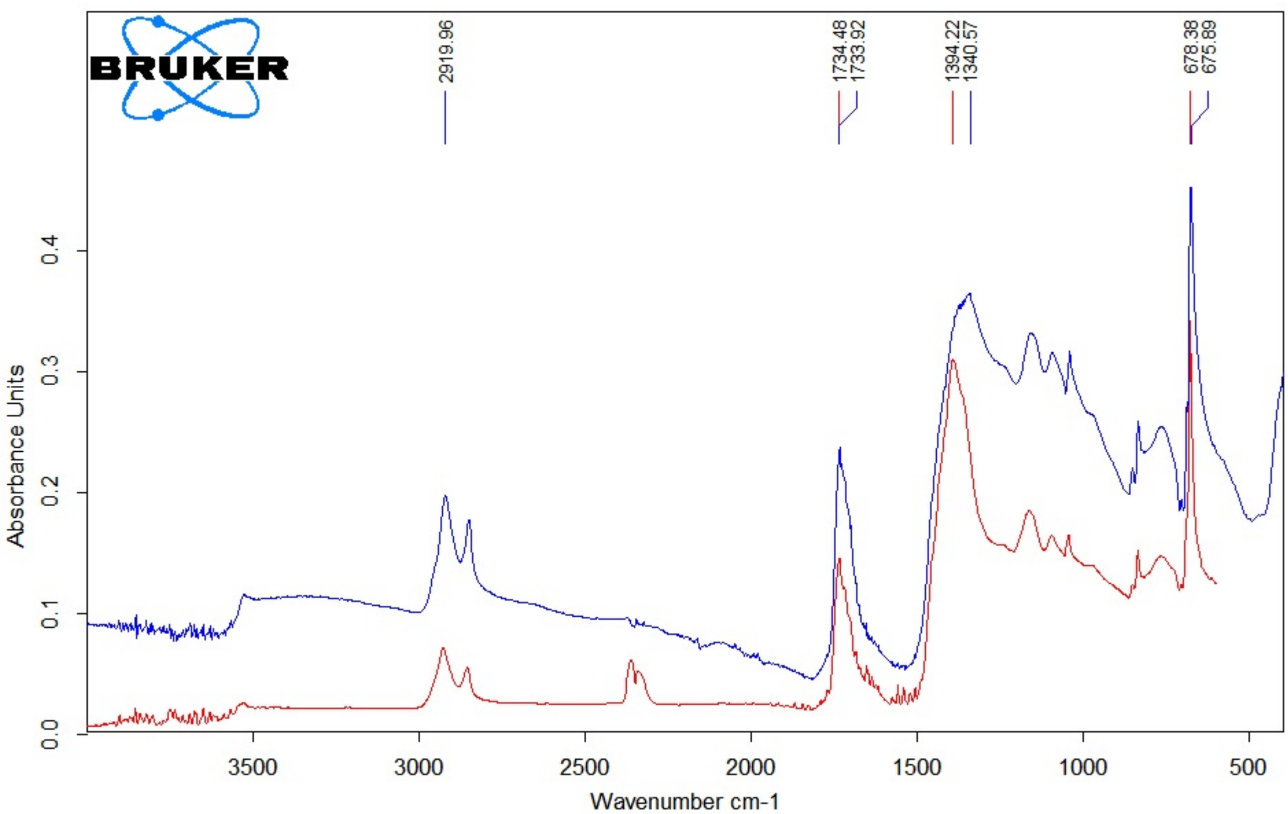
CHEMICAL COMPOUNDS:

$Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$

$2PbCO_3 \cdot Pb(OH)_2$

RECIPE ORIGIN: Hezekial Reynolds

Alpha-P & Hyperion Spectrum



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Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 8, Navy Blue

PIGMENTS:

Prussian Blue, Lead White

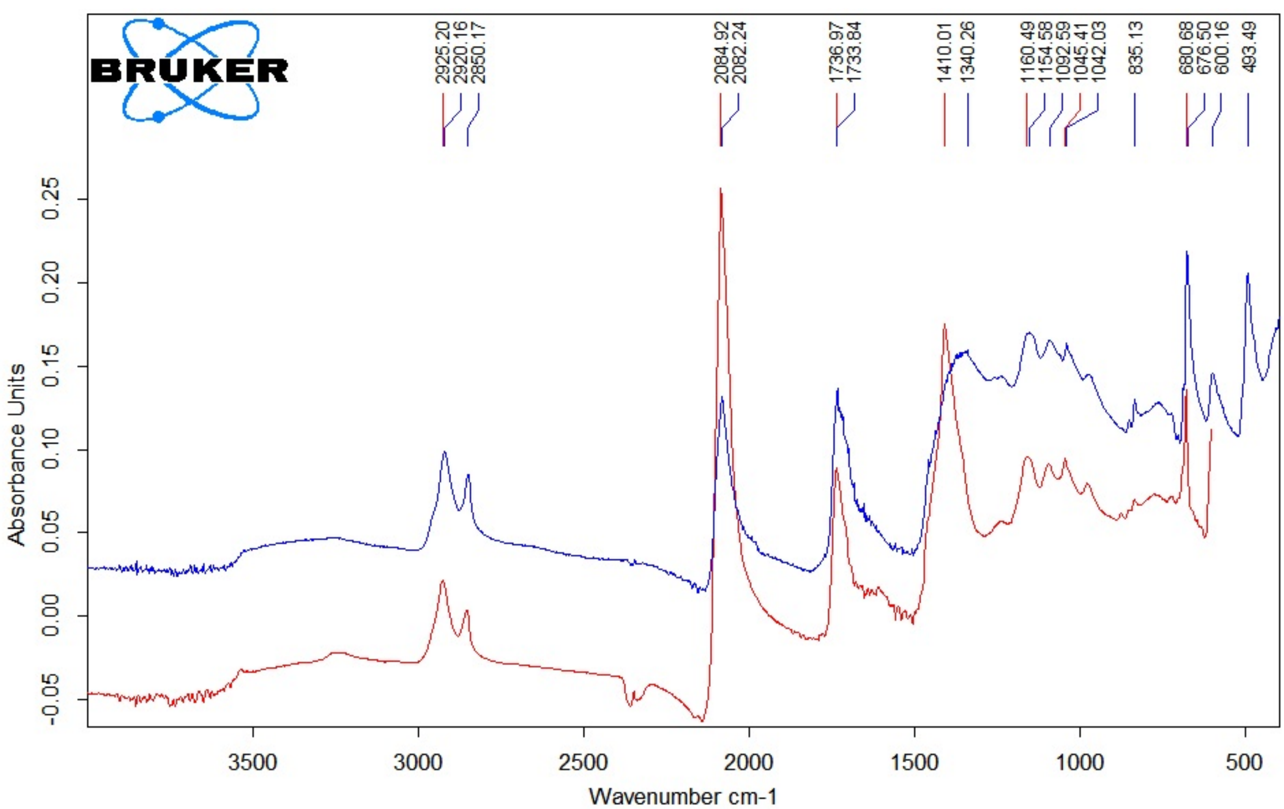
CHEMICAL COMPOUNDS:

$Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$

$2PbCO_3 \cdot Pb(OH)_2$

RECIPE ORIGIN: Hezekial Reynolds

Alpha-P & Hyperion Spectrum



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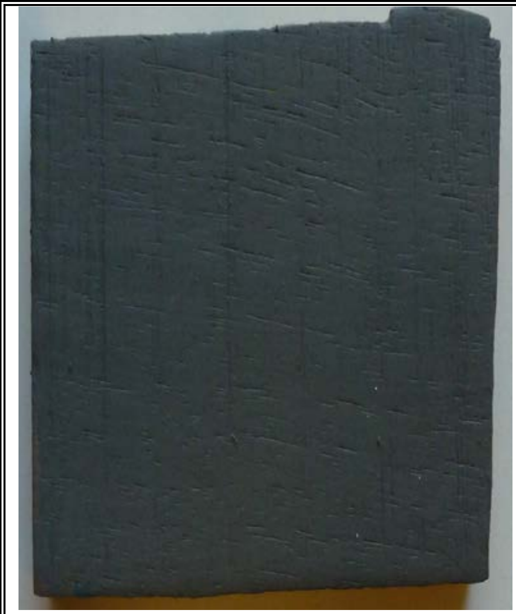


Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 9, Dark Stone Color

PIGMENTS:

Lead White, Yellow Ochre, Lamp Black

CHEMICAL COMPOUNDS:

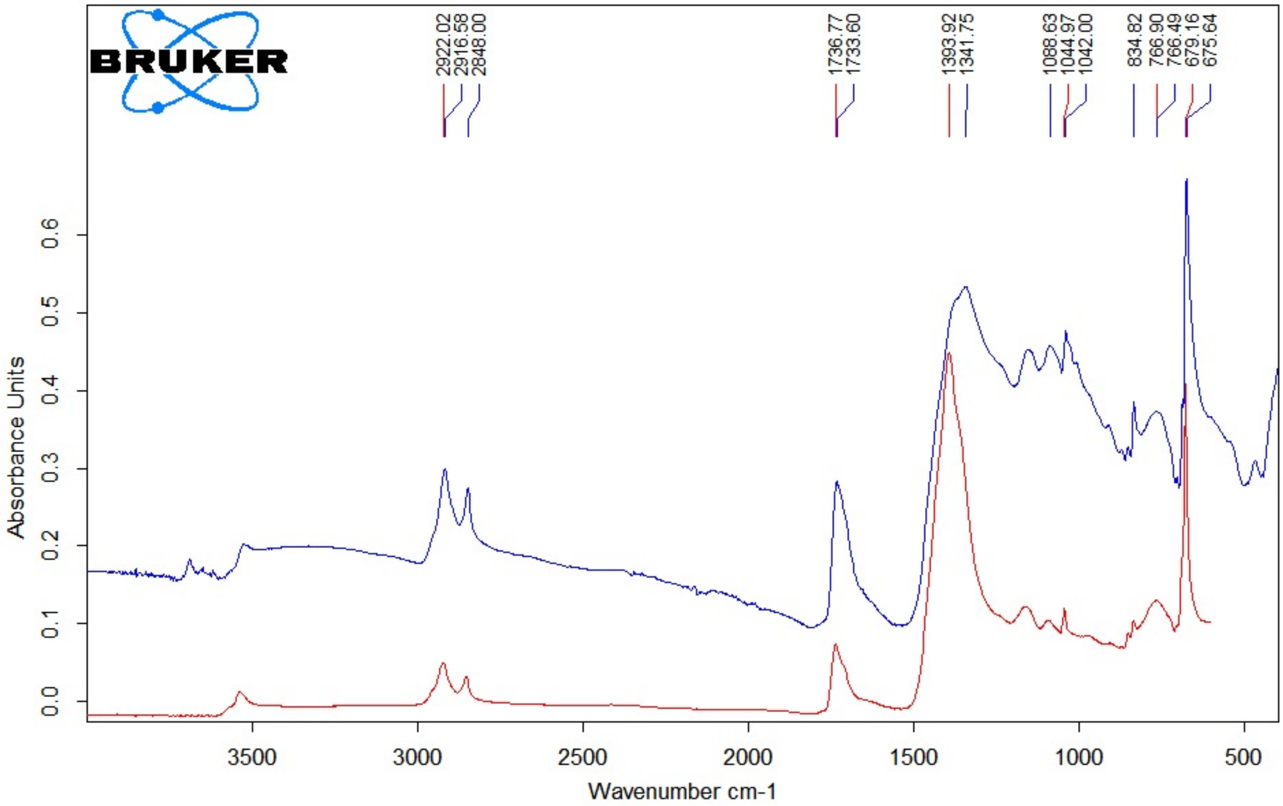
$2PbCO_3 \cdot Pb(OH)_2$

FeO(OH))

C

RECIPE ORIGIN: Hezekial Reynolds

Alpha-P & Hyperion Spectrum



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C:\Users\User\Desktop\THESIS\Spectra\03.13.13 Hyperion\sample-9.0	Sample-9	Hyperion reflectance		3/13/2013

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Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 10, Red Color 1

PIGMENTS:

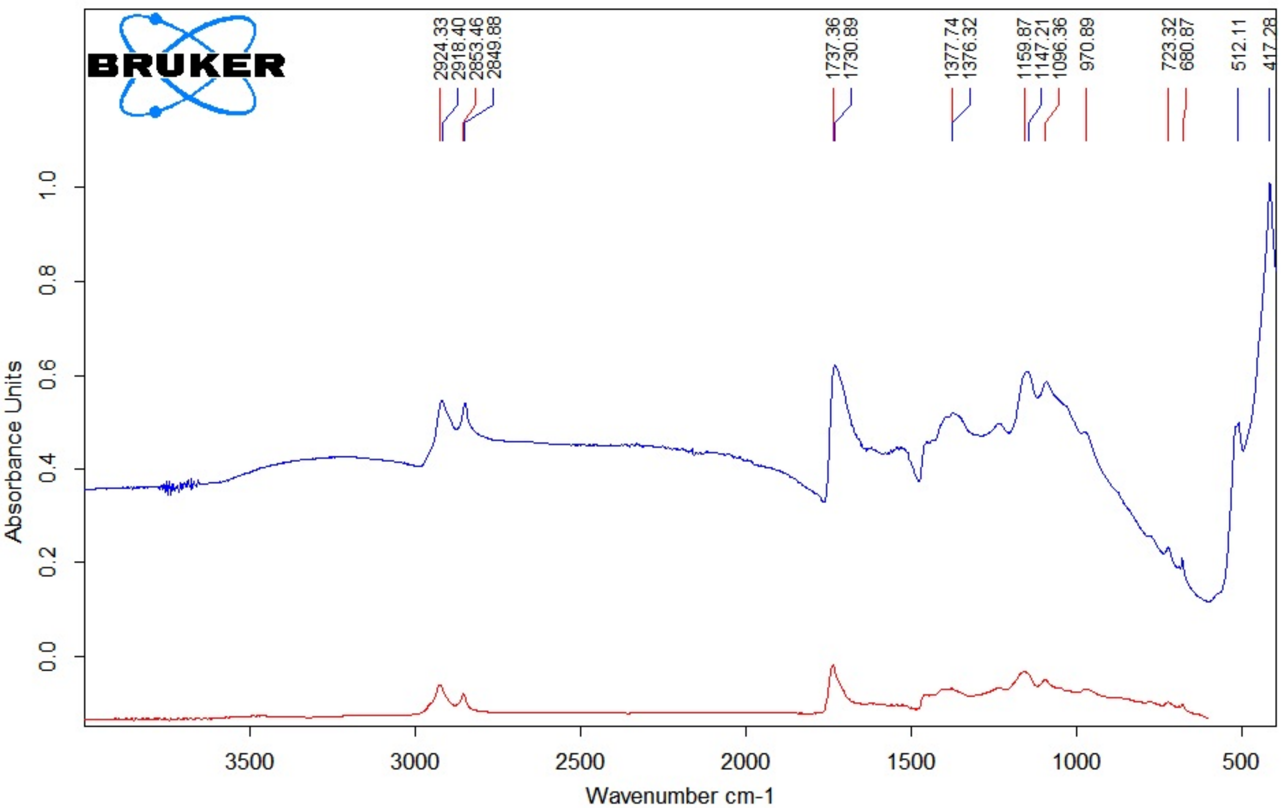
Red Lead ground in oil

CHEMICAL COMPOUNDS:

Pb_3O_4

RECIPE ORIGIN: Hezekial Reynolds

Alpha-P & Hyperion Spectrum



C:\Users\User\Desktop\THESIS\Spectra\03.13.13 Hyperion\sample-10.0	Sample-10	Hyperion reflectance		3/13/2013
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Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 11

PIGMENTS:

Chrome Yellow Deep, Lead White, $CaCO_3$

CHEMICAL COMPOUNDS:

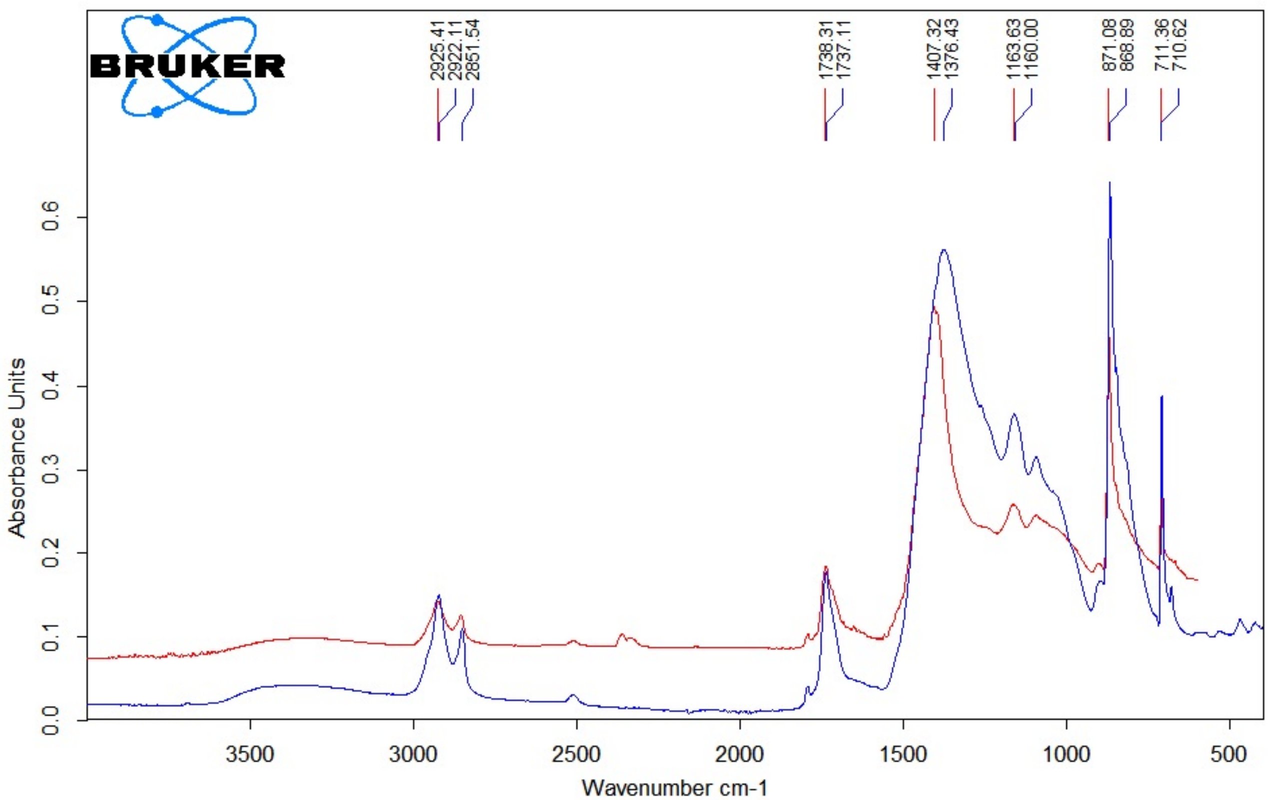
$PbCrO_4$

$2\ PbCO_3 \cdot Pb(OH)_2$

$CaCO_3$

RECIPE ORIGIN: NA

Alpha-P & Hyperion Spectrum



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Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 12, Dark Ice Color

PIGMENTS:

Lead White, Rosin, Verdigris, Lampblack

CHEMICAL COMPOUNDS:

$2\ PbCO_3 \cdot Pb(OH)_2$

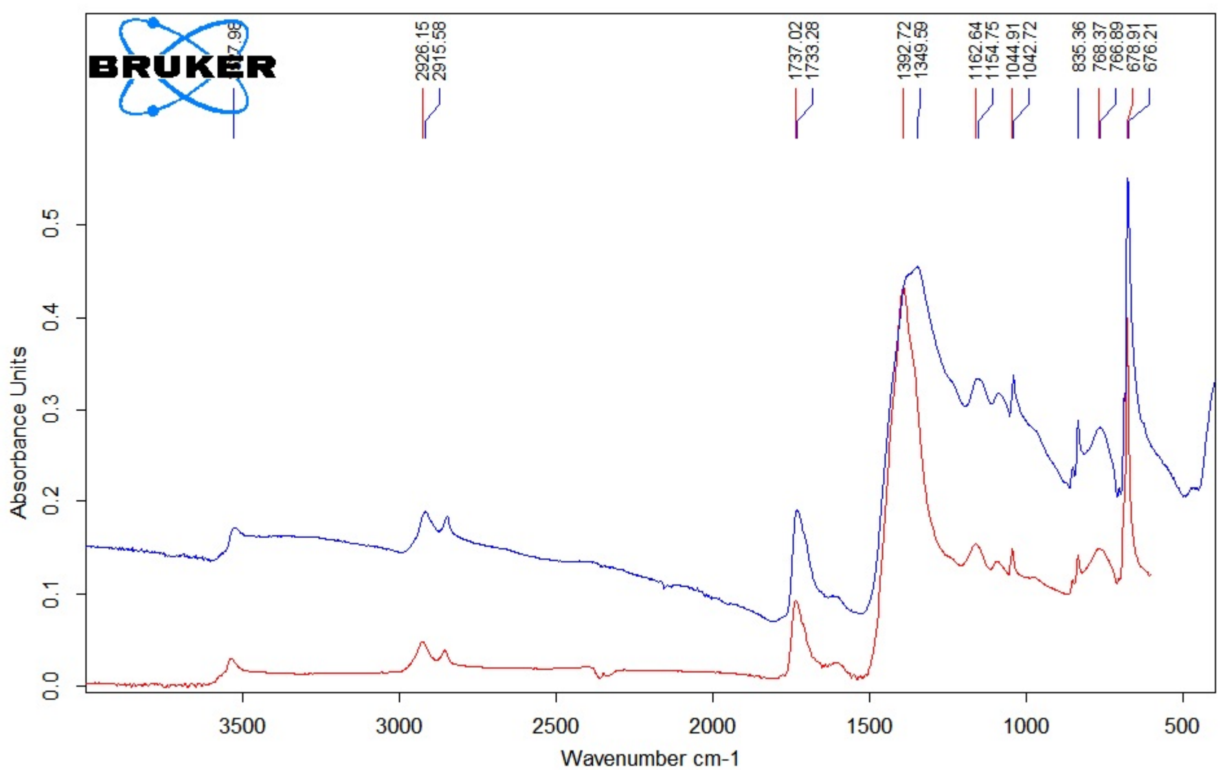
$C_{15}H_{20}O_6$

$Cu(OH)_2 \cdot (CH_3COO)_2 \cdot 5\ H_2$

C

RECIPE ORIGIN: Hezekial Reynolds

Alpha-P & Hyperion Spectrum



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Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 13, Claret Color

PIGMENTS:

Lead White, Spanish Brown (Caput Mortuum), Lampblack

CHEMICAL COMPOUNDS:

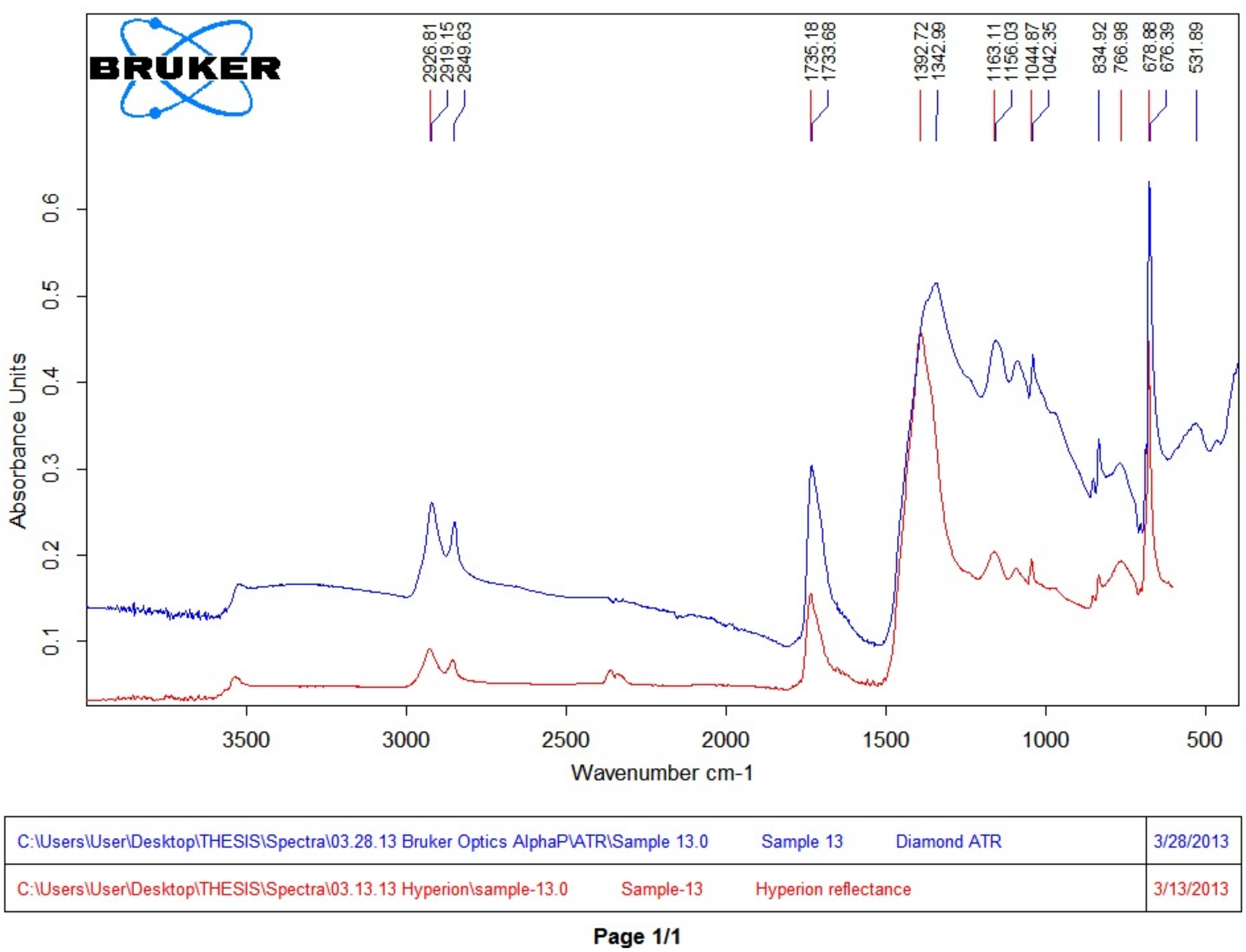
$2\ PbCO_3 \cdot Pb(OH)_2$

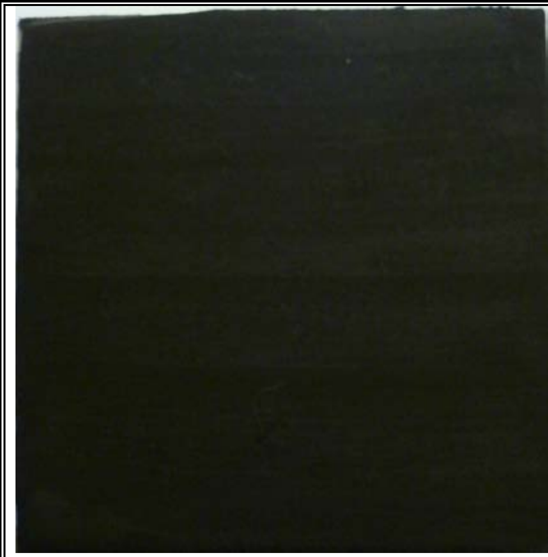
Fe_2O_3

C

RECIPE ORIGIN: Hezekial Reynolds

Alpha-P & Hyperion Spectrum





Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 14, Chocolate Color

PIGMENTS:

Spanish Brown (Caput Mortuum), Lampblack

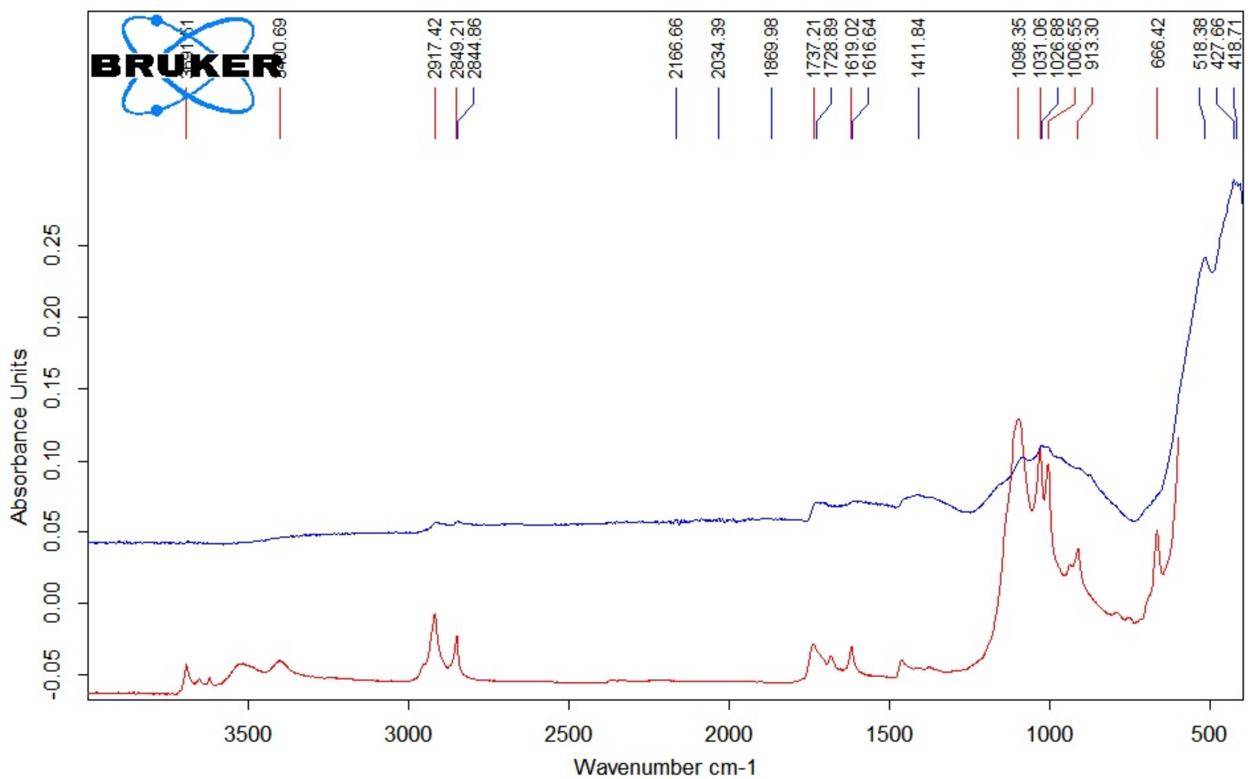
CHEMICAL COMPOUNDS:

Fe_2O_3

C

RECIPE ORIGIN: Hezekial Reynolds

Alpha-P & Hyperion Spectrum



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Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 15

PIGMENTS:

Chrome Yellow Deep, $CaCO_3$

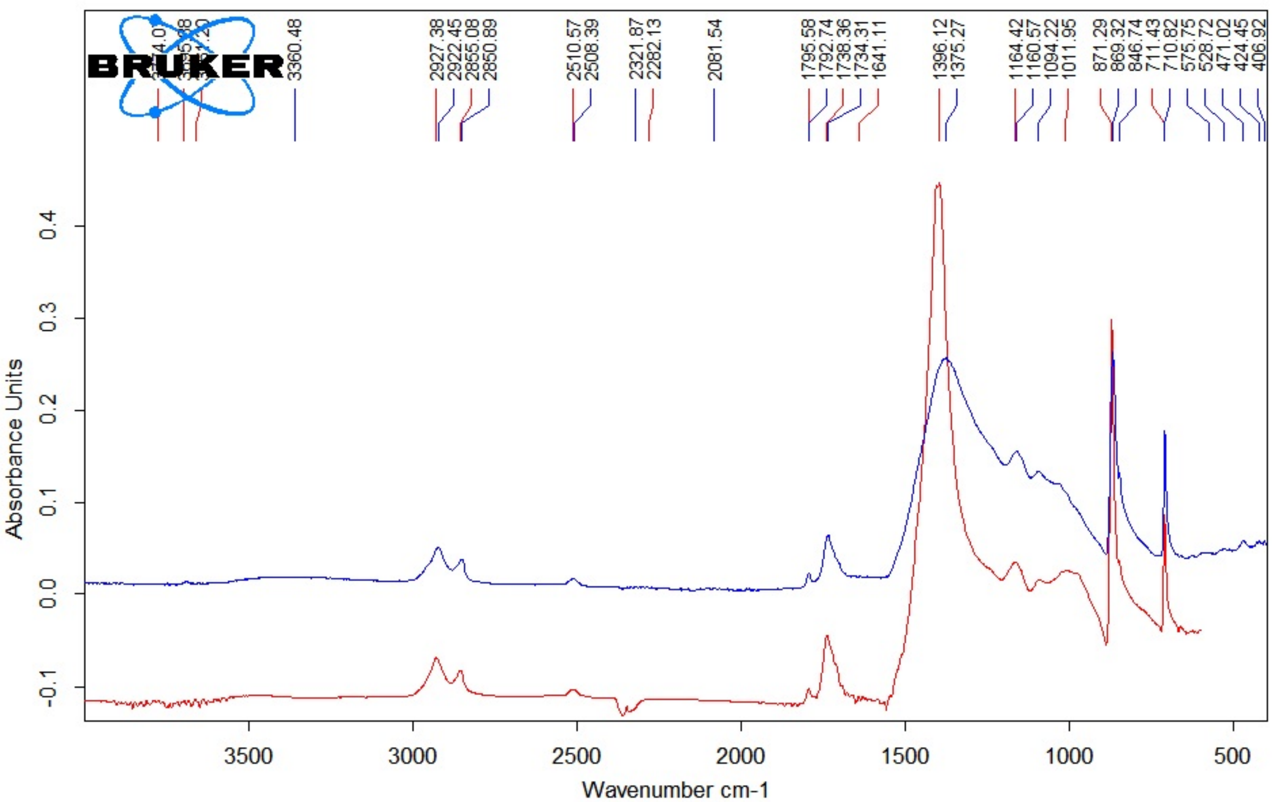
CHEMICAL COMPOUNDS:

$PbCrO_4$

$CaCO_3$

RECIPE ORIGIN: Susan Buck

Alpha-P & Hyperion Spectrum



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C:\Users\User\Desktop\THESIS\Spectra\03.13.13 Hyperion\sample-15.0	Sample-15	Hyperion reflectance		3/13/2013

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Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 16

PIGMENTS:

Yellow Ochre, Lead White, $CaCO_3$

CHEMICAL COMPOUNDS:

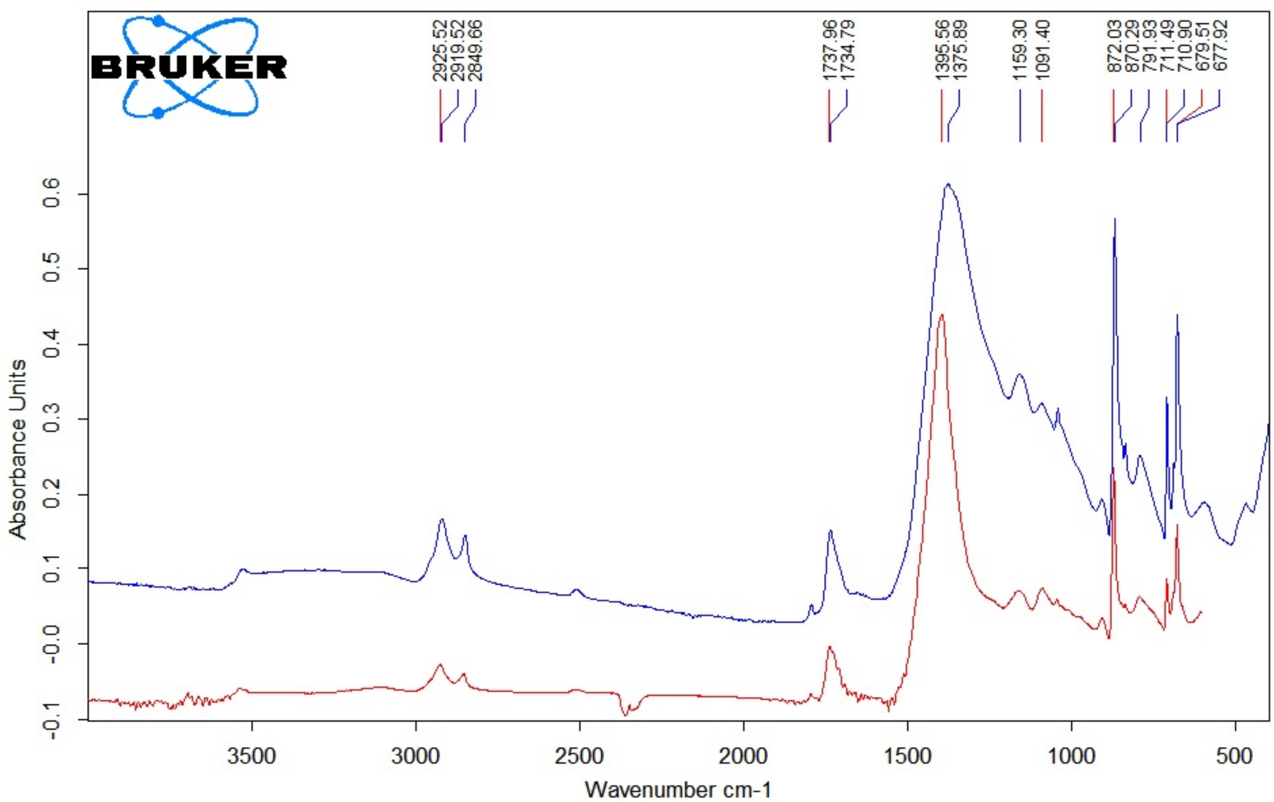
$2\ PbCO_3 \cdot Pb(OH)_2$

FeO(OH))

$CaCO_3$

RECIPE ORIGIN: Susan Buck

Alpha-P & Hyperion Spectrum



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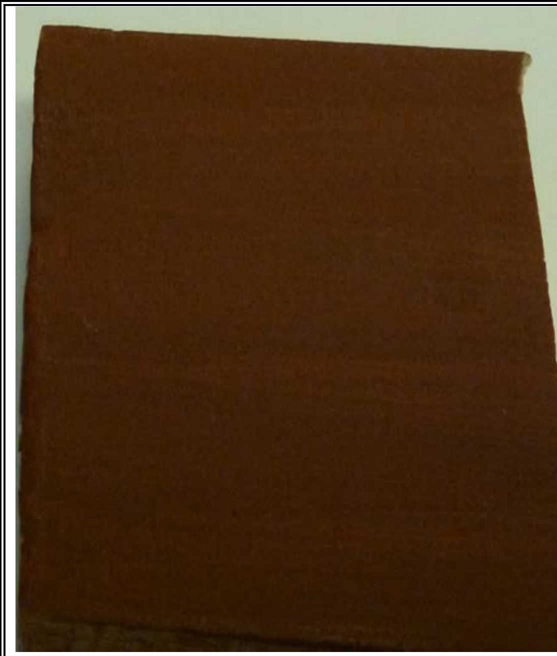


Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 17

PIGMENTS:

Spanish Brown (Caput Mortuum), Red Lead, $CaCO_3$

CHEMICAL COMPOUNDS:

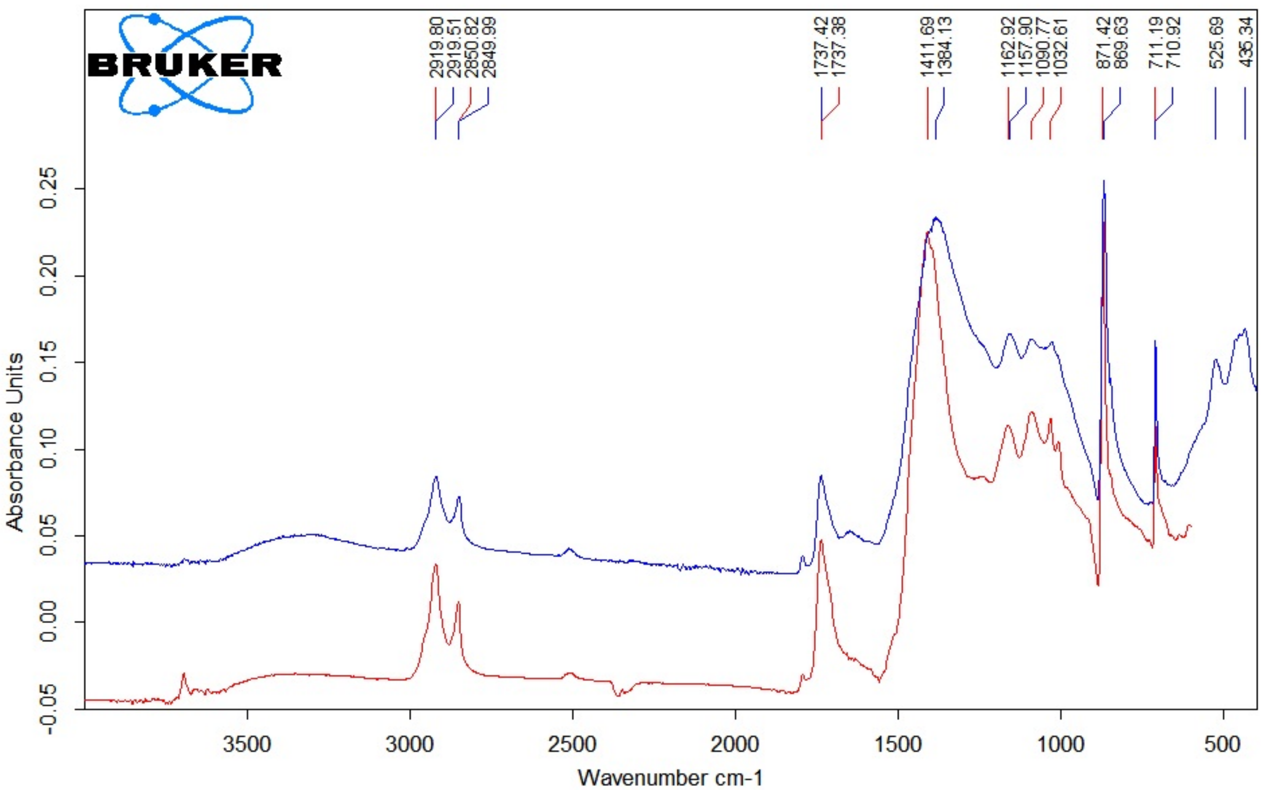
Fe_2O_3

Pb_3O_4

$CaCO_3$

RECIPE ORIGIN: Susan Buck

Alpha-P & Hyperion Spectrum



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C:\Users\User\Desktop\THESIS\Spectra\03.13.13 Hyperion\sample-17.0	Sample-17	Hyperion reflectance	3/13/2013

Page 1/1

Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 18, Red Color 2

PIGMENTS:

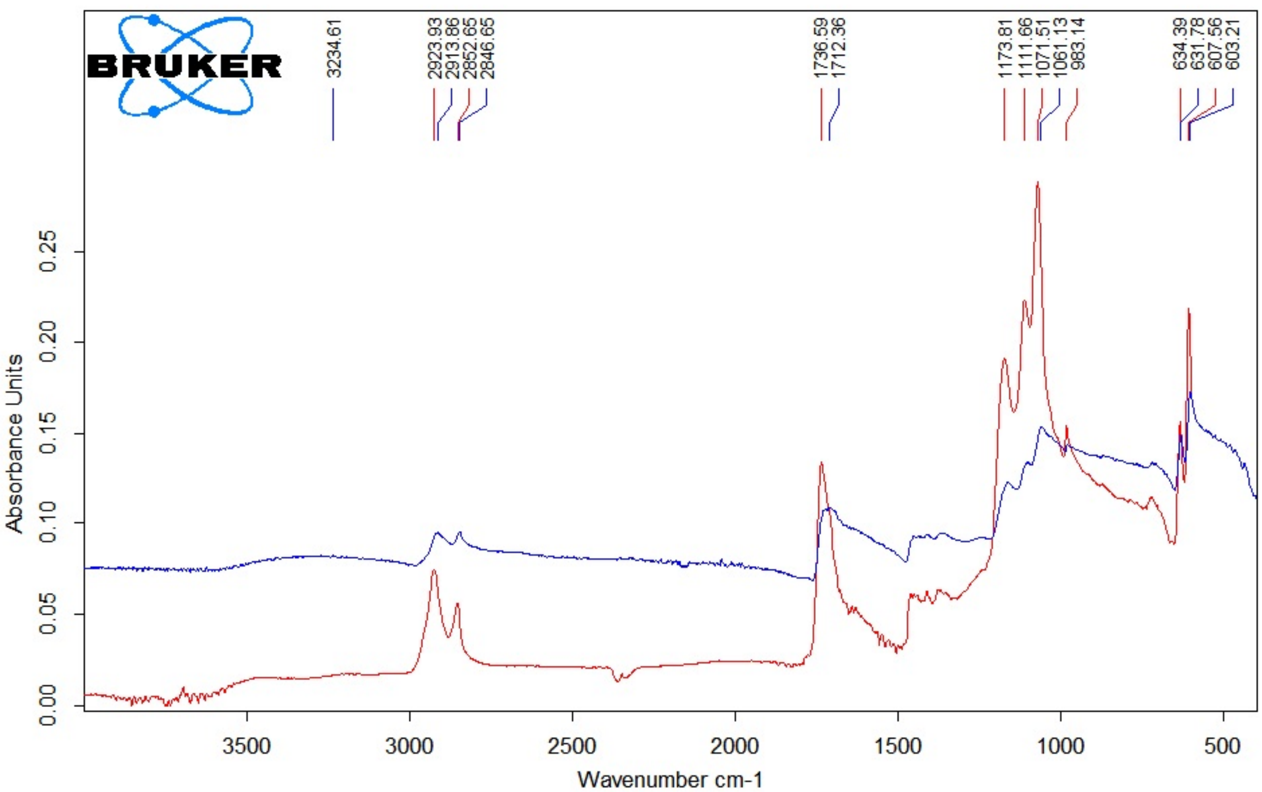
Vermilion ground in oil

CHEMICAL COMPOUNDS:

HgS

RECIPE ORIGIN: Hezekial Reynolds

Alpha-P & Hyperion Spectrum



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C:\Users\User\Desktop\THESIS\Spectra\03.13.13 Hyperion\sample-18.0	Sample-18	Hyperion reflectance	3/13/2013

Page 1/1

Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 19, Light Ice Color

PIGMENTS:

small amount of Dark Ice Color (Lead White, Rosin, Verdigris, Lampblack), White Lead

CHEMICAL COMPOUNDS:

2 $PbCO_3 \cdot Pb(OH)_2$

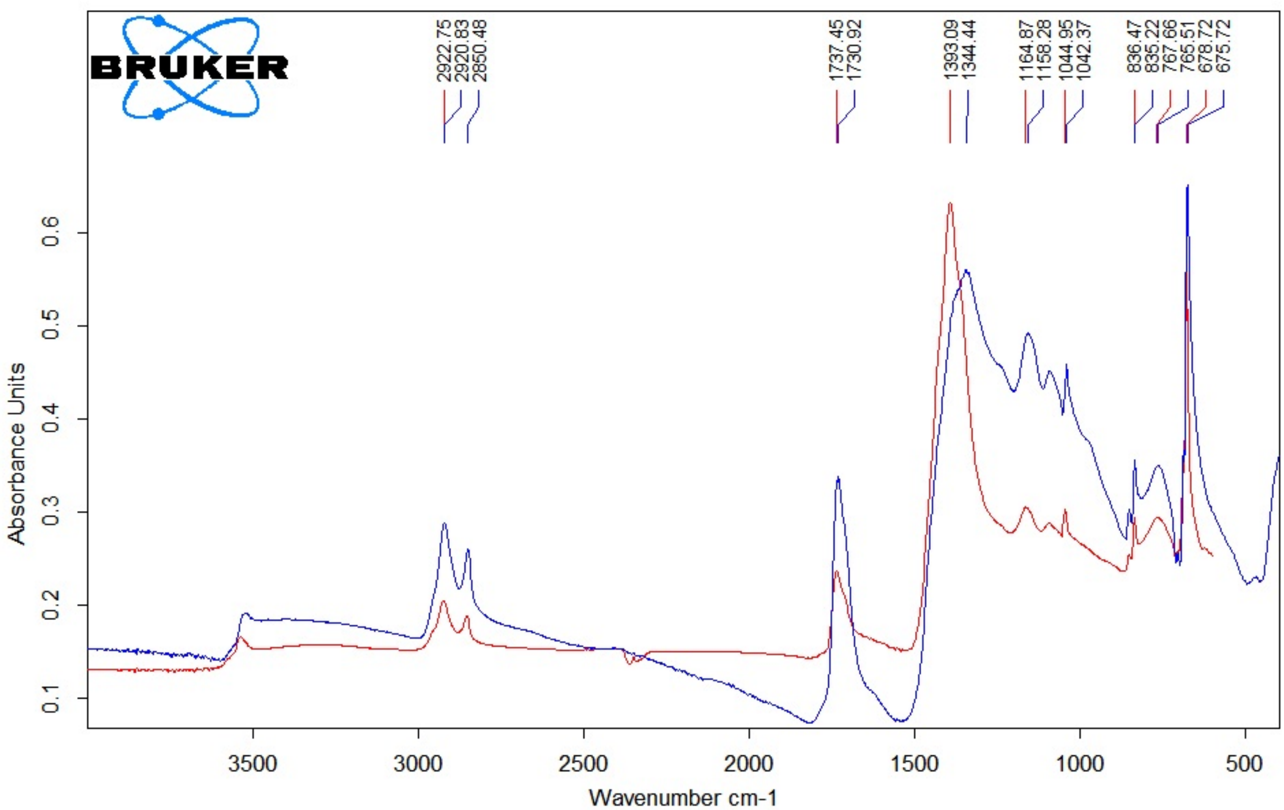
$C_{15}H_{20}O_6$

$Cu(OH)_2 \cdot (CH_3COO)_2 \cdot 5\ H_2$

C

RECIPE ORIGIN: Hezekial Reynolds

Alpha-P & Hyperion Spectrum



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C:\Users\User\Desktop\THESIS\Spectra\03.13.13 Hyperion\sample-19.0	Sample-19	Hyperion reflectance	3/13/2013

Page 1/1

Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 20, Purple Color

PIGMENTS:

Rose Pink (Brazil Wood Lake on $CaCO_3$), Prussian Blue

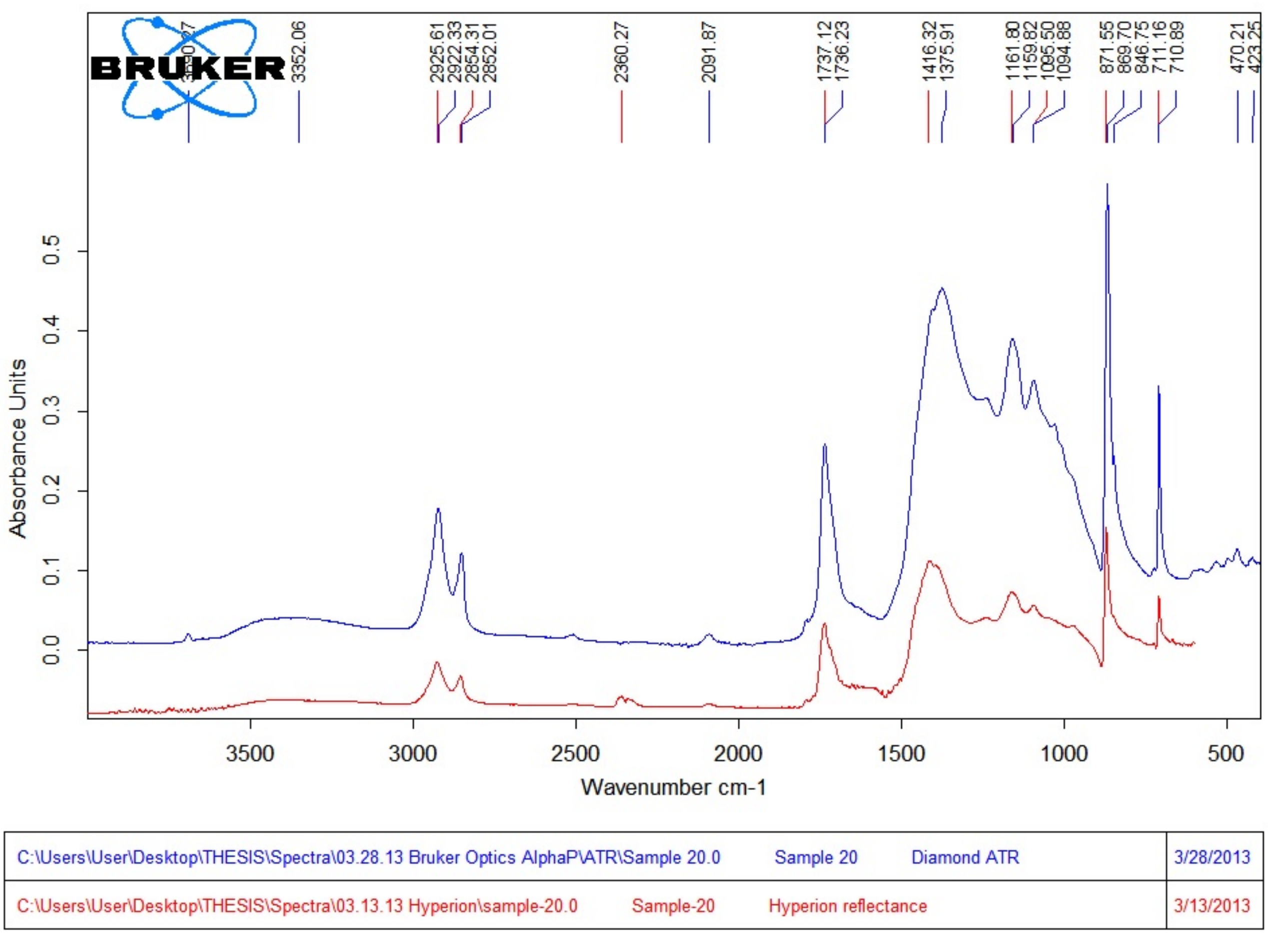
CHEMICAL COMPOUNDS:

$C_{16}H_{14}O_5$, $C_{16}H_{12}O_5$ dried onto $CaCO_3$

$Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$

RECIPE ORIGIN: Hezekial Reynolds

Alpha-P & Hyperion Spectrum



Page 1/1

Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 21

PIGMENTS:

Lead White, $CaCO_3$

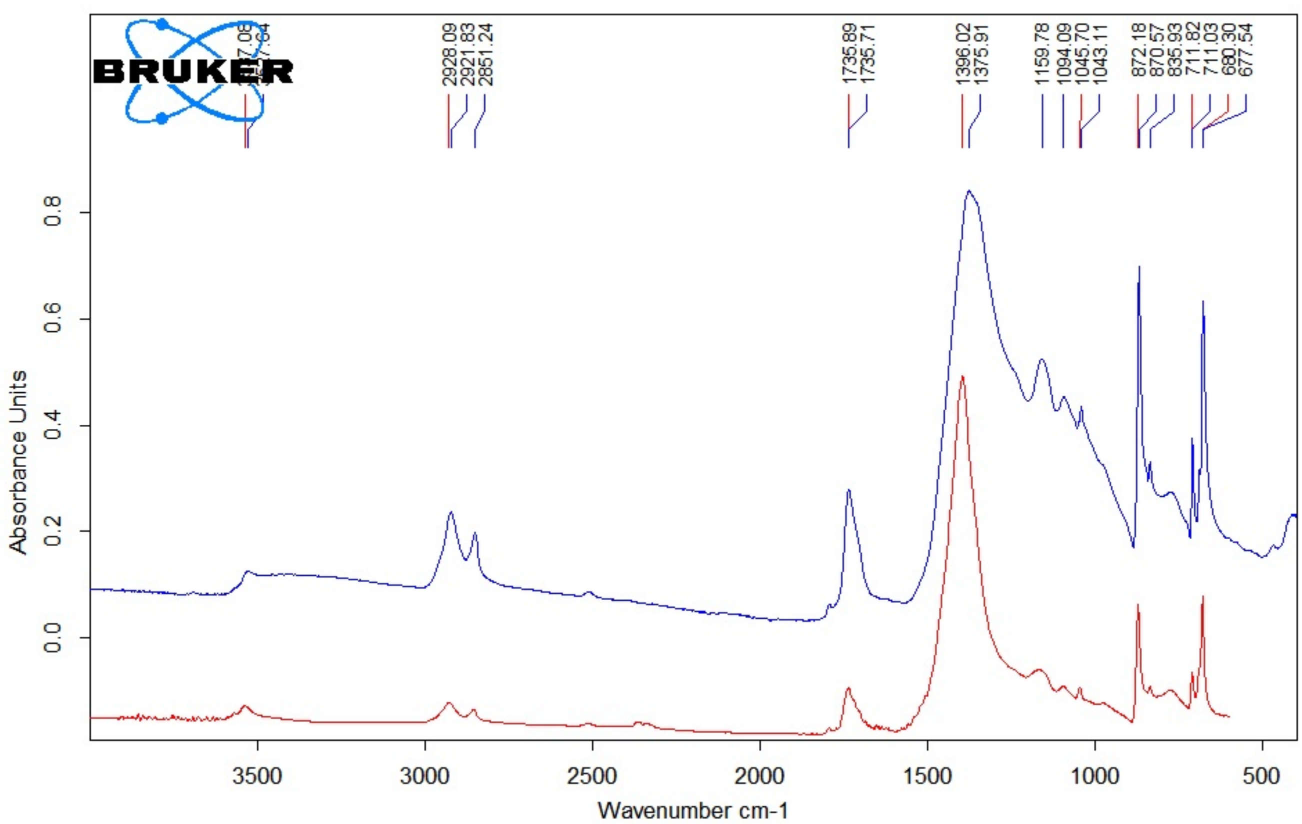
CHEMICAL COMPOUNDS:

$CaCO_3$

2 $PbCO_3 \cdot Pb(OH)_2$

RECIPE ORIGIN: Susan Buck

Alpha-P & Hyperion Spectrum



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C:\Users\User\Desktop\THESIS\Spectra\03.13.13 Hyperion\sample-21.0	Sample-21	Hyperion reflectance		3/13/2013

Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 22

PIGMENTS:

Lead White, Verdigris

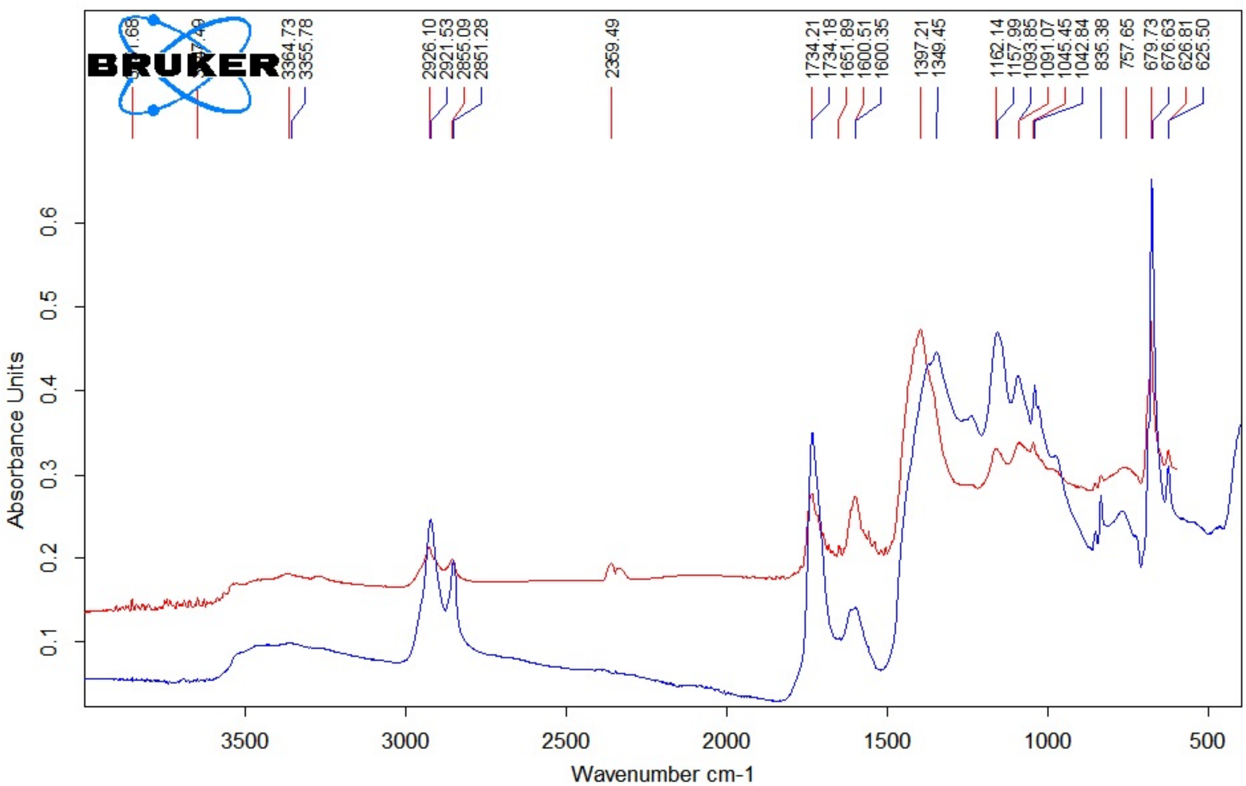
CHEMICAL COMPOUNDS:

$2\ PbCO_3 \cdot Pb(OH)_2$

$Cu(OH)_2 \cdot (CH_3COO)_2 \cdot 5\ H_2O$

RECIPE ORIGIN: NA

Alpha-P & Hyperion Spectrum



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C:\Users\User\Desktop\THESIS\Spectra\03.13.13 Hyperion\sample-22.0	Sample-22	Hyperion reflectance	3/13/2013

Page 1/1

Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

SAMPLE #: 23

PIGMENTS:

Venetian Lead, Lead White

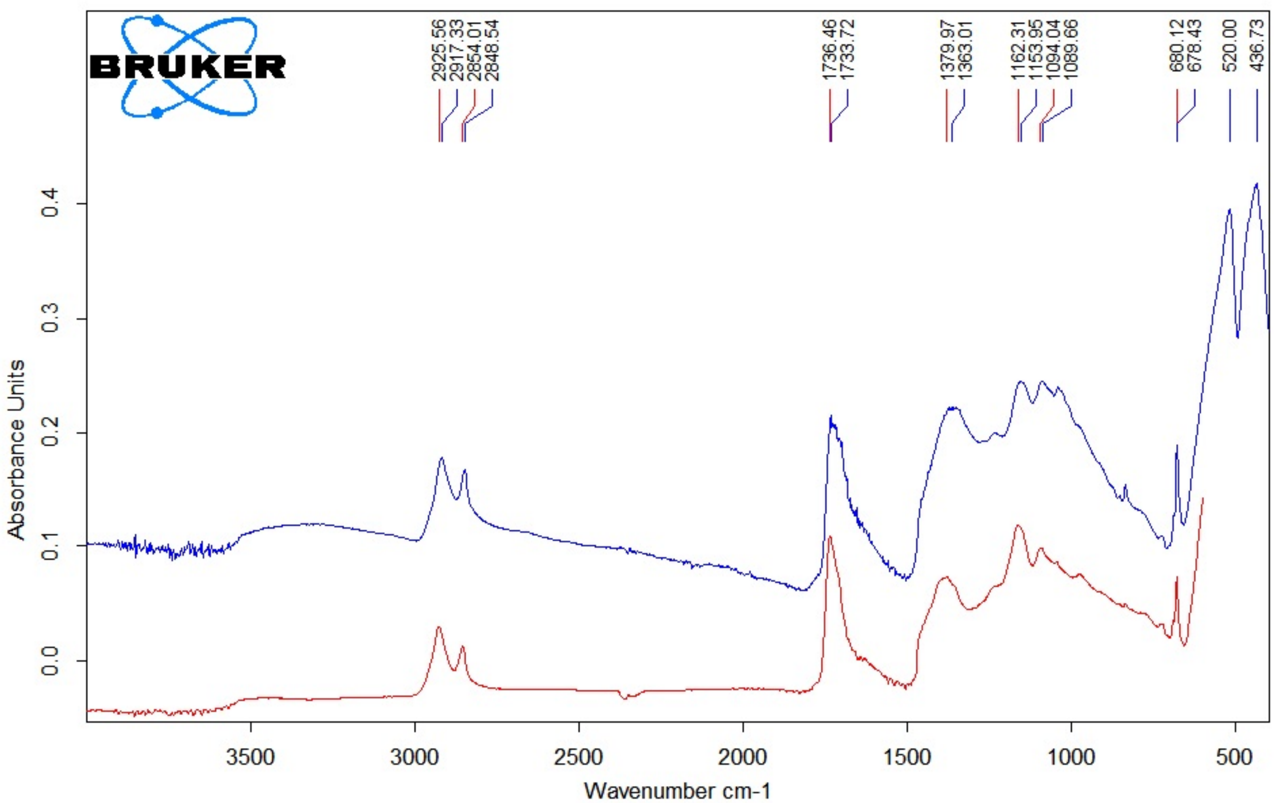
CHEMICAL COMPOUNDS:

$CaFe_2O_7S$

$2\ PbCO_3 \cdot Pb(OH)_2$

RECIPE ORIGIN: NA

Alpha-P & Hyperion Spectrum



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C:\Users\User\Desktop\THESIS\Spectra\03.13.13 Hyperion\sample-23.0	Sample-23	Hyperion reflectance		3/13/2013

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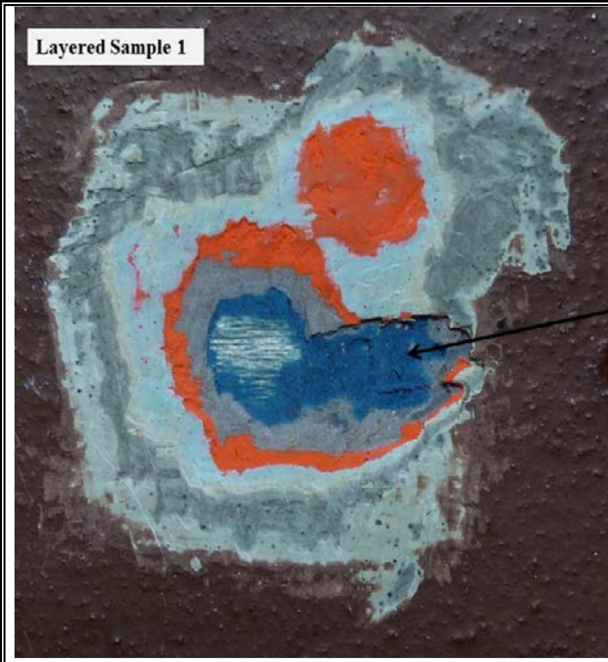
Appendix 2: Layered Control Samples Information & Spectra



Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

LAYERED SAMPLE 1, Layer 1

Navy

PIGMENTS:

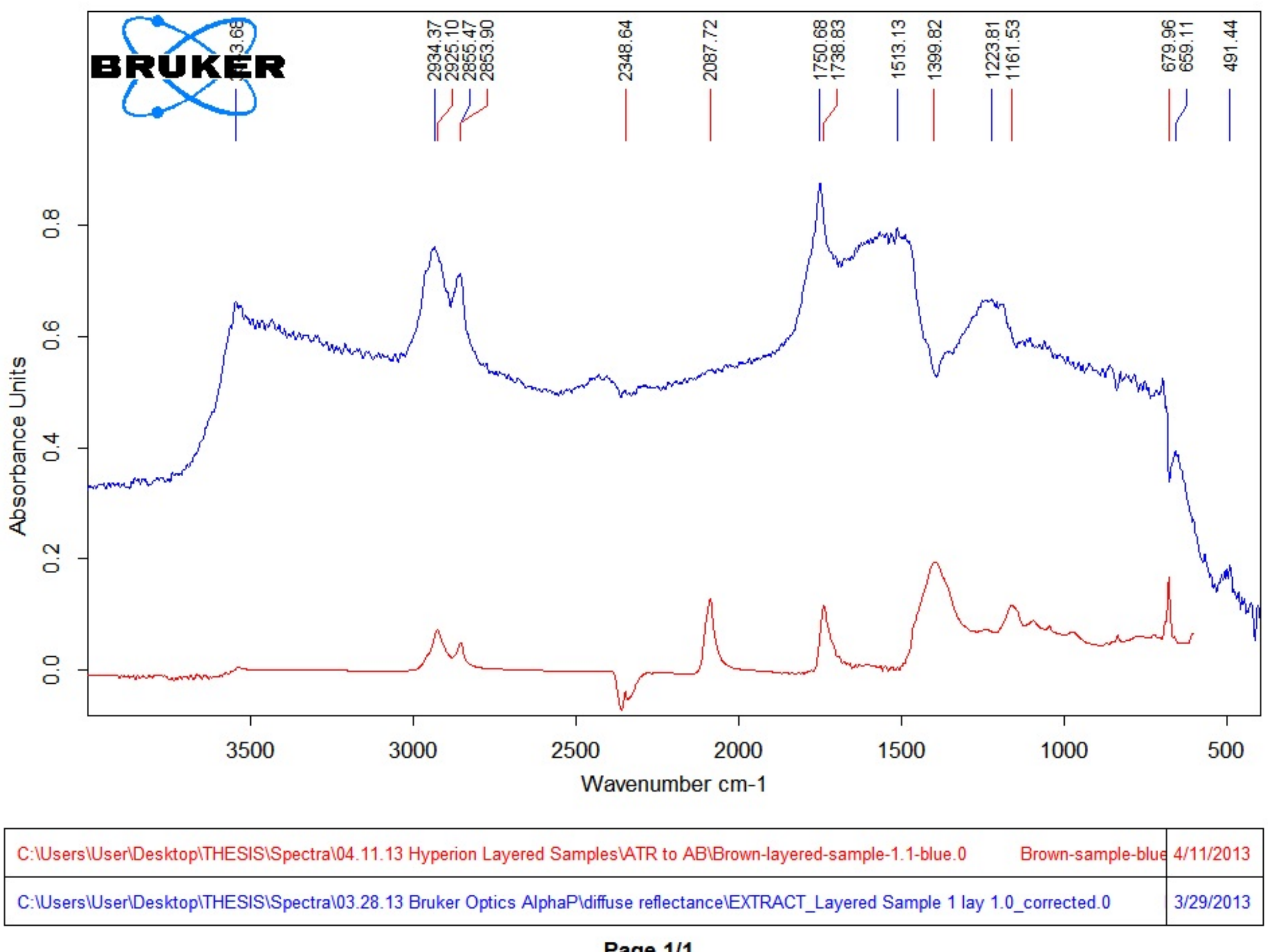
Prussian Blue & Lead White

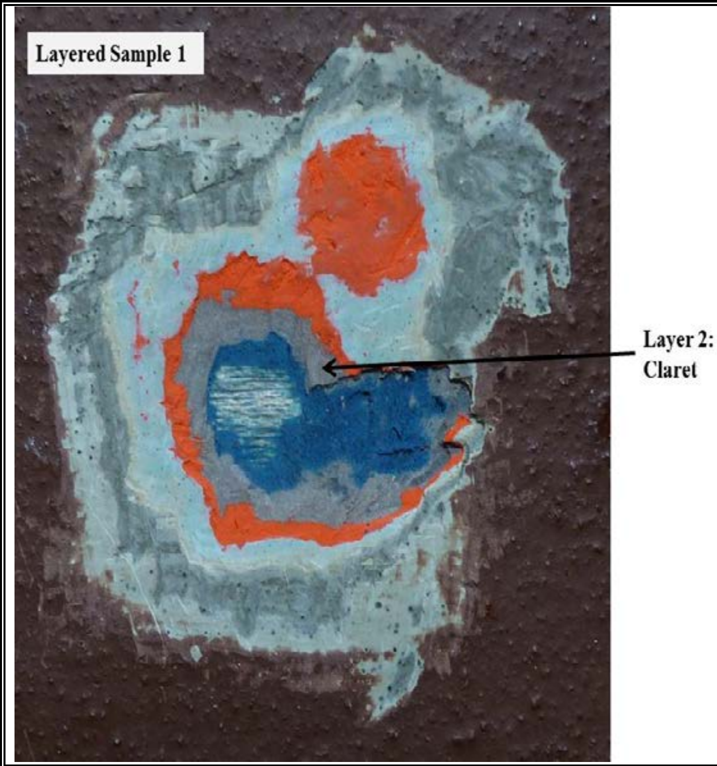
CHEMICAL COMPOUNDS:

$Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$

$2PbCO_3 \cdot Pb(OH)_2$

Alpha-P & Hyperion Spectrum



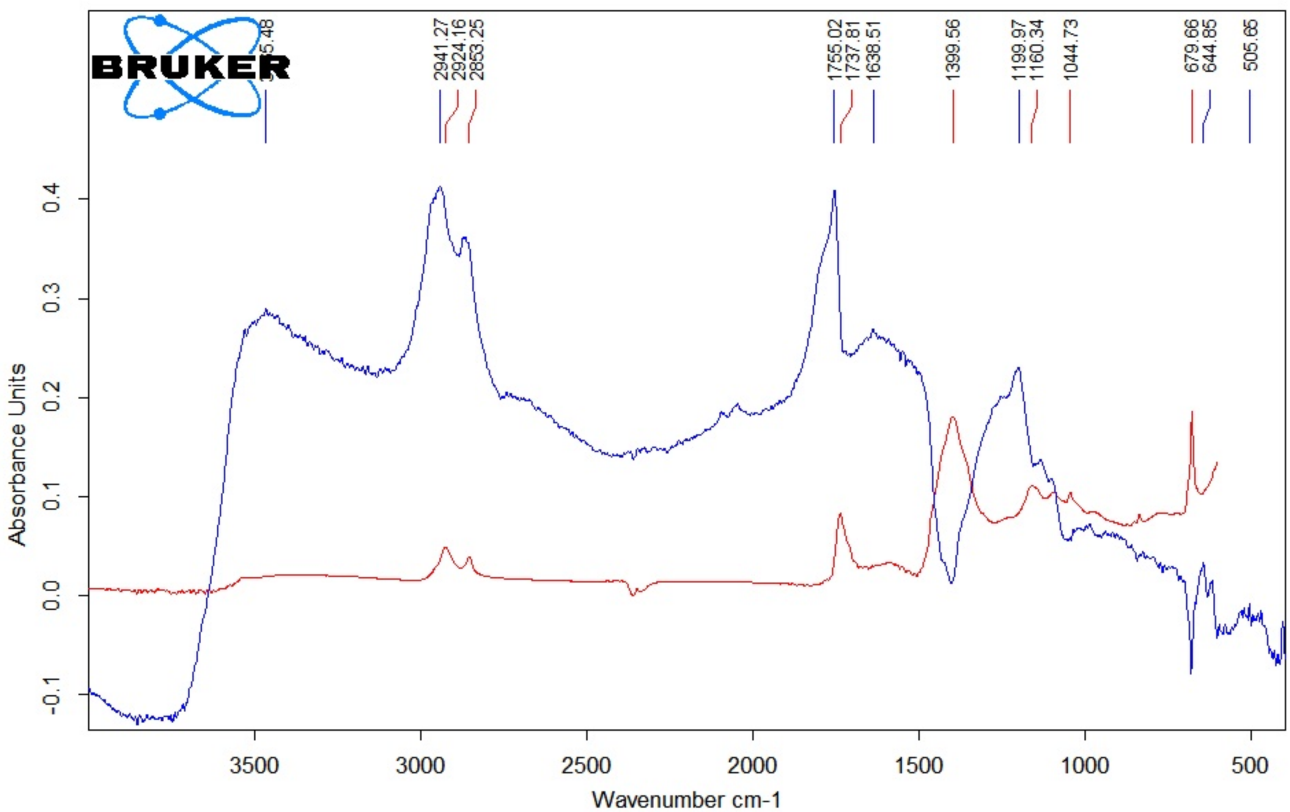


Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

LAYERED SAMPLE 1, Layer 2
Claret
PIGMENTS:
White Lead, Spanish Brown (Caput Mortuum), Lampblack
CHEMICAL COMPOUNDS:
2 $PbCO_3 \cdot Pb(OH)_2$
Fe_2O_3
C

Alpha-P & Hyperion Spectrum



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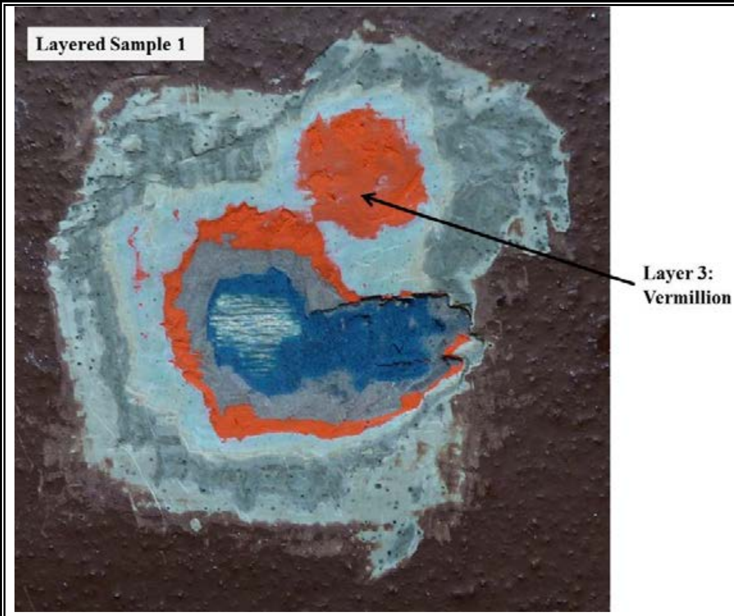
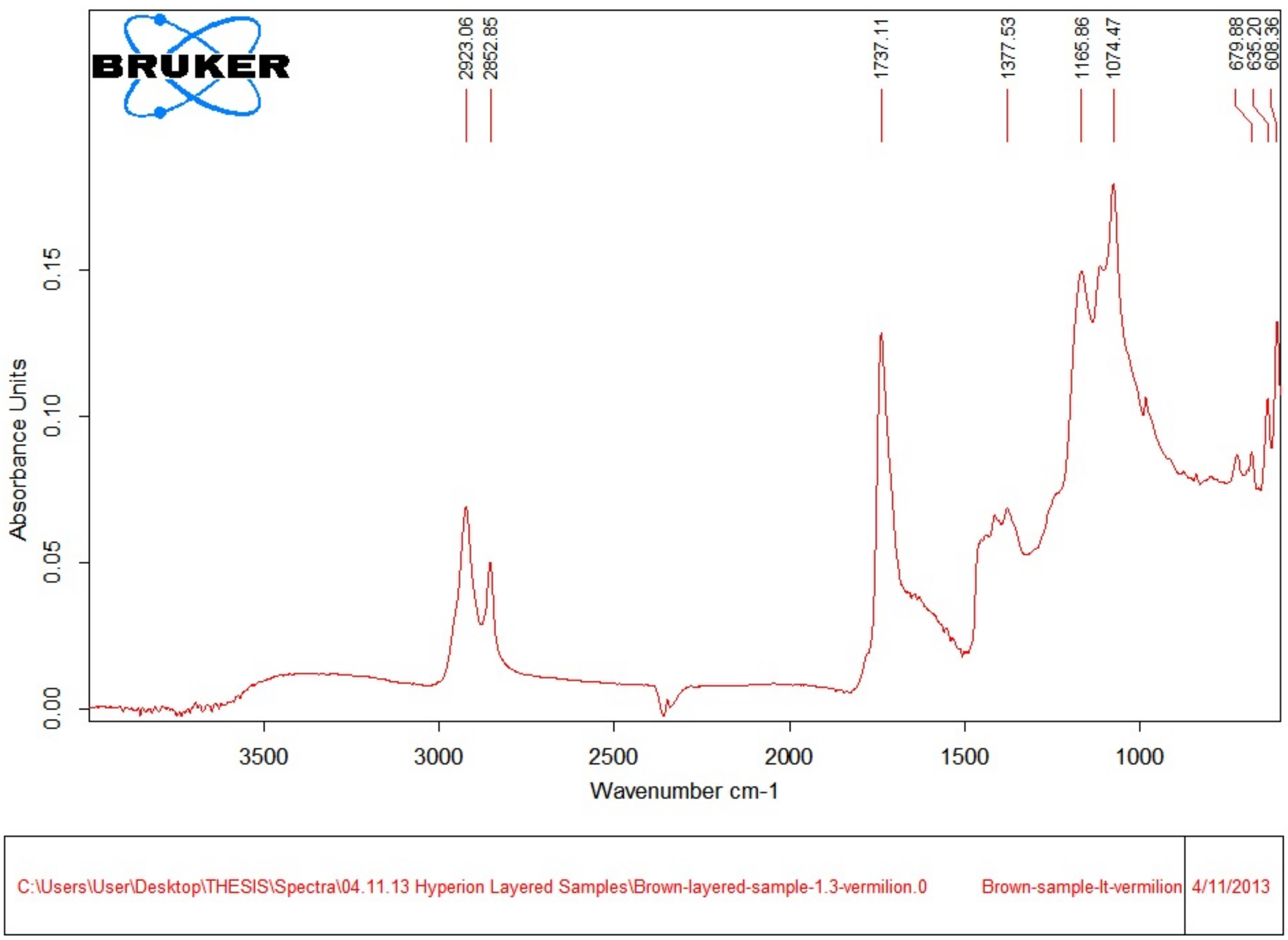


Control Sample Data Sheet

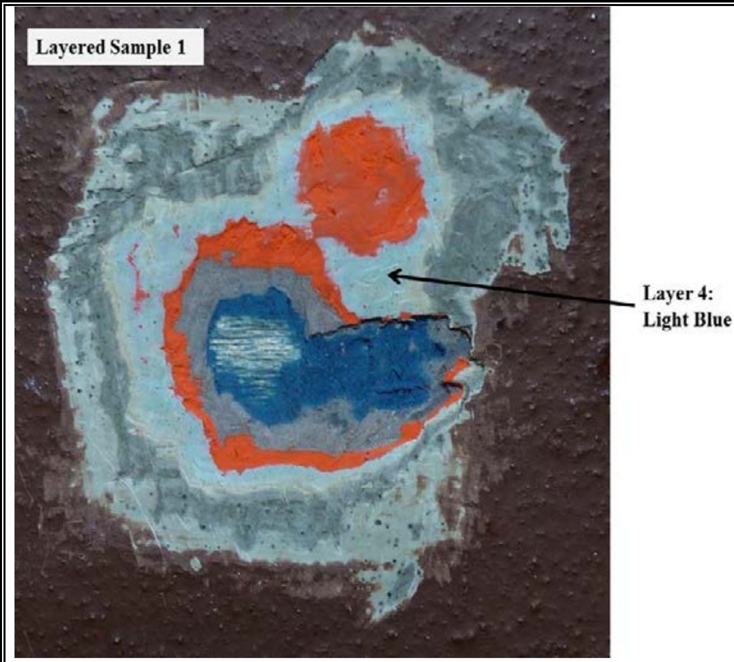
All samples are on wood and pigments are in raw linseed oil

LAYERED SAMPLE 1, Layer 3
Vermillion
PIGMENTS:
Vermillion ground in oil
CHEMICAL COMPOUNDS:
HgS

Hyperion Spectrum



Page 1/1

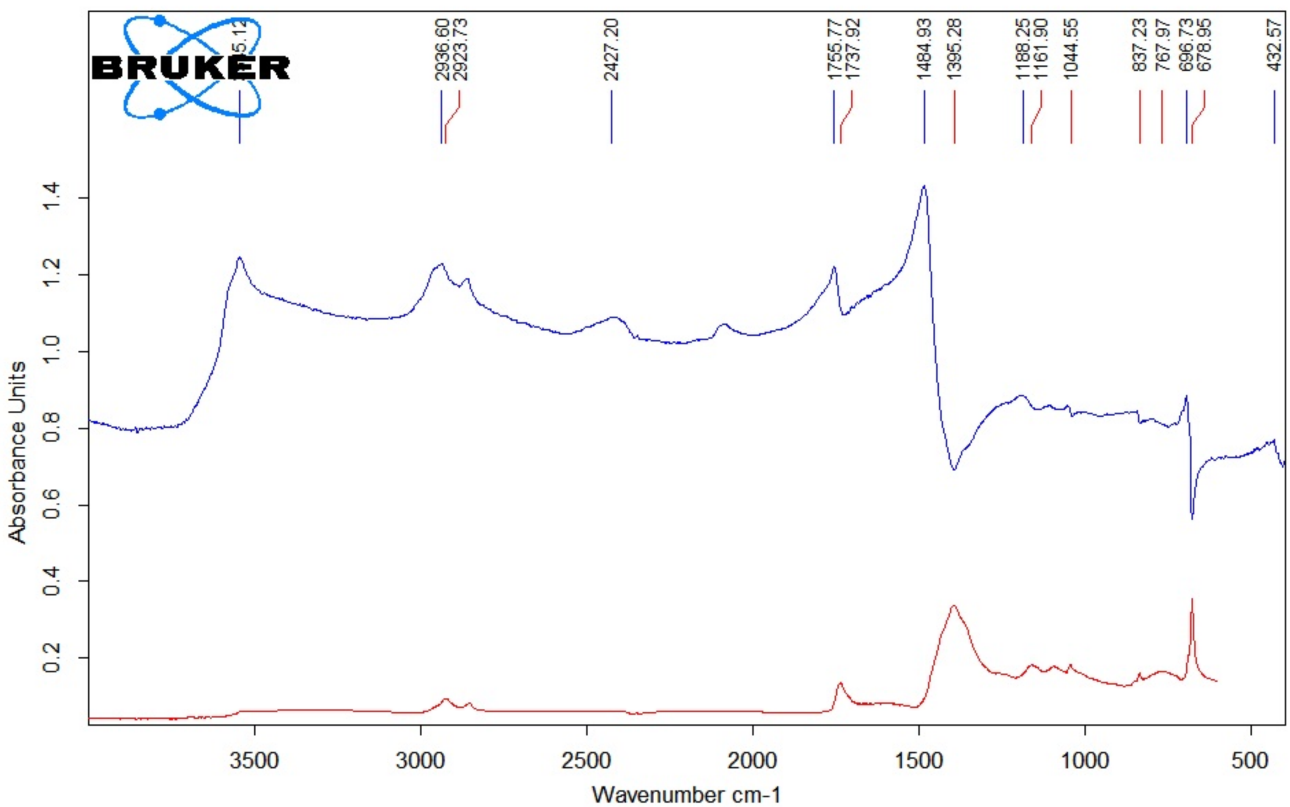


Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

LAYERED SAMPLE 1, Layer 4
Light/Sky Blue
PIGMENTS:
Prussian Blue, Lead White
CHEMICAL COMPOUNDS:
$Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$
$2PbCO_3 \cdot Pb(OH)_2$

Alpha-P & Hyperion Spectrum



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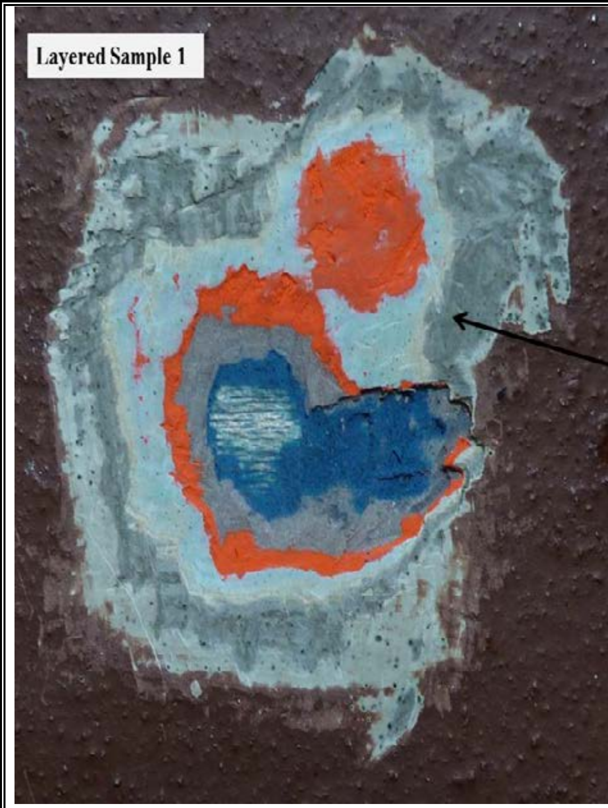
C:\Users\User\Desktop\THESIS\Spectra\04.11.13 Hyperion Layered Samples\Brown-layered-sample-1.4-ltblue.0	Brown-sample-lt-blue H	4/11/2013

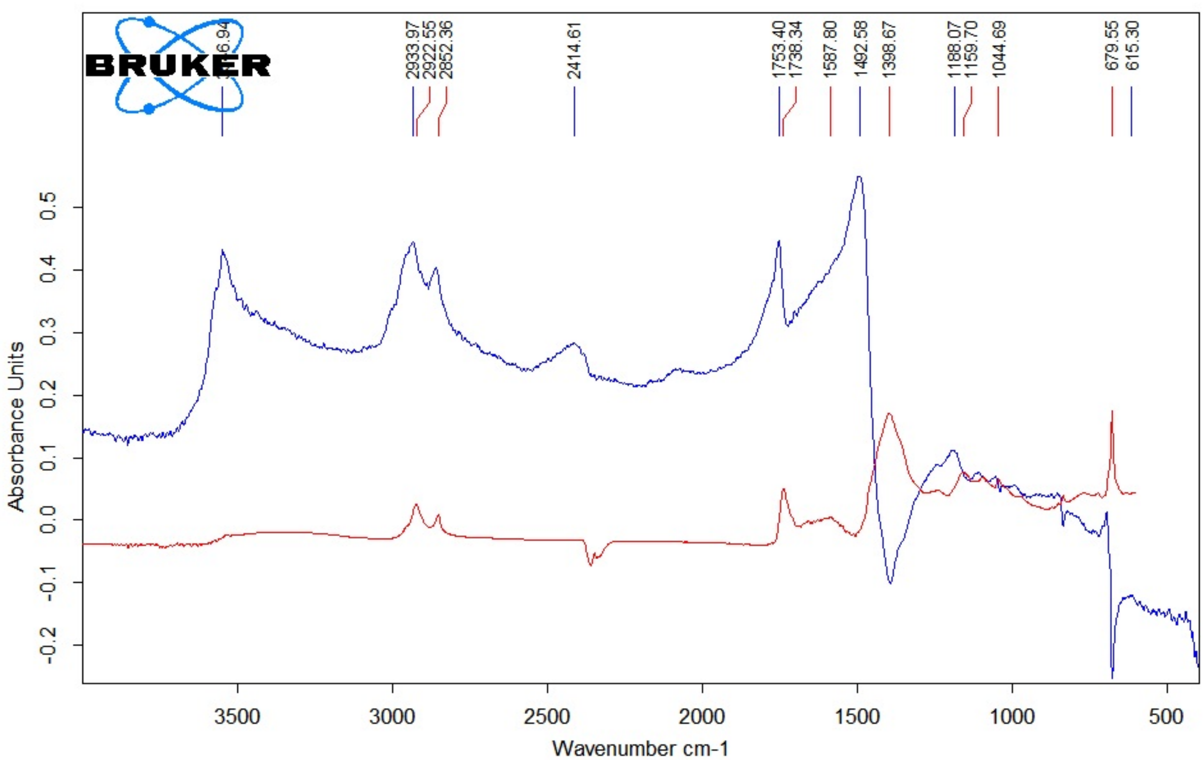


Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

LAYERED SAMPLE 1, Layer 5
Dark Ice
PIGMENTS:
Lead White, Rosin, Verdigris, Lampblack
CHEMICAL COMPOUNDS:
$2\ PbCO_3 \cdot Pb(OH)_2$
$C_{15}H_{20}O_6$
$Cu(OH)_2 \cdot (CH_3COO)_2 \cdot 5\ H_2$
C

Alpha-P & Hyperion Spectrum



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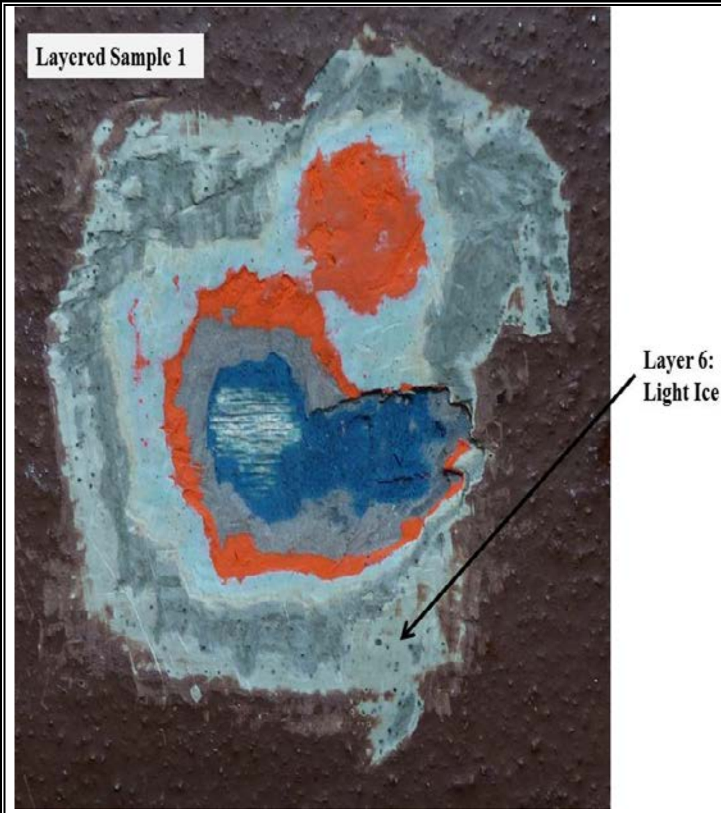
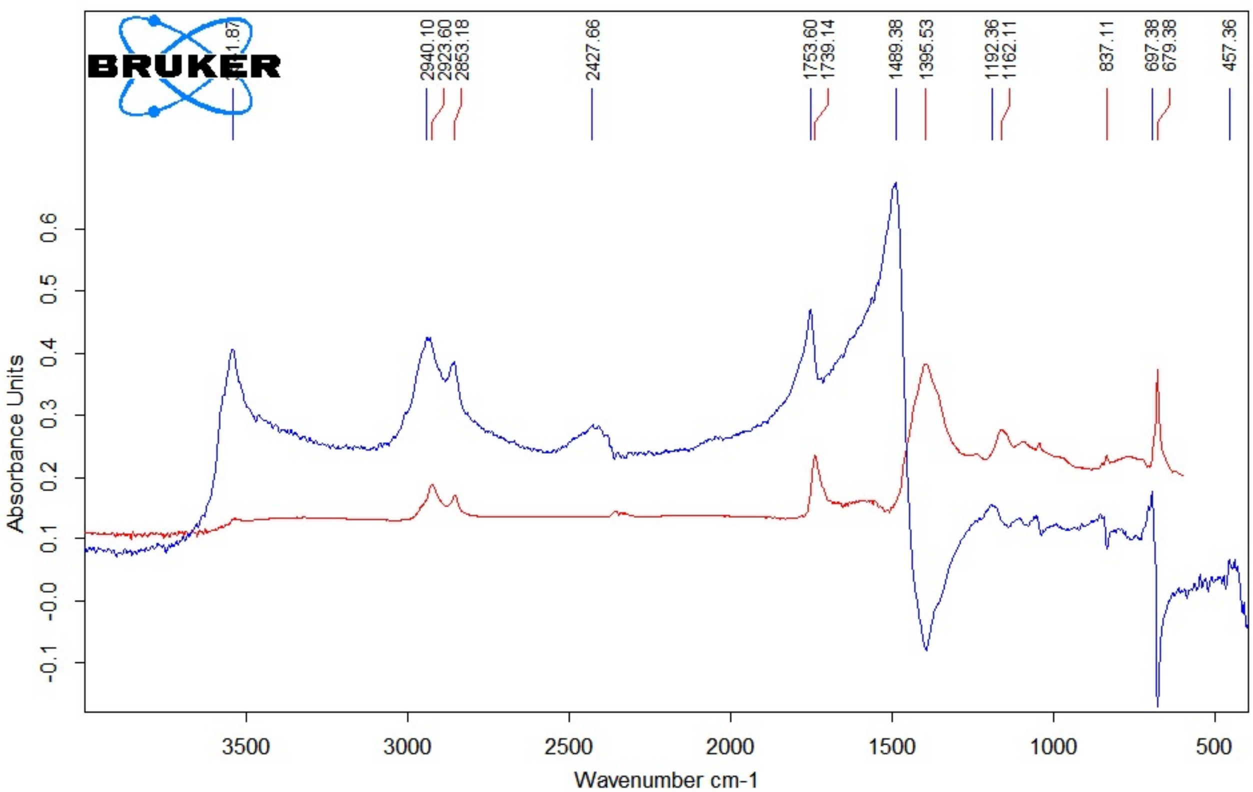


Control Sample Data Sheet

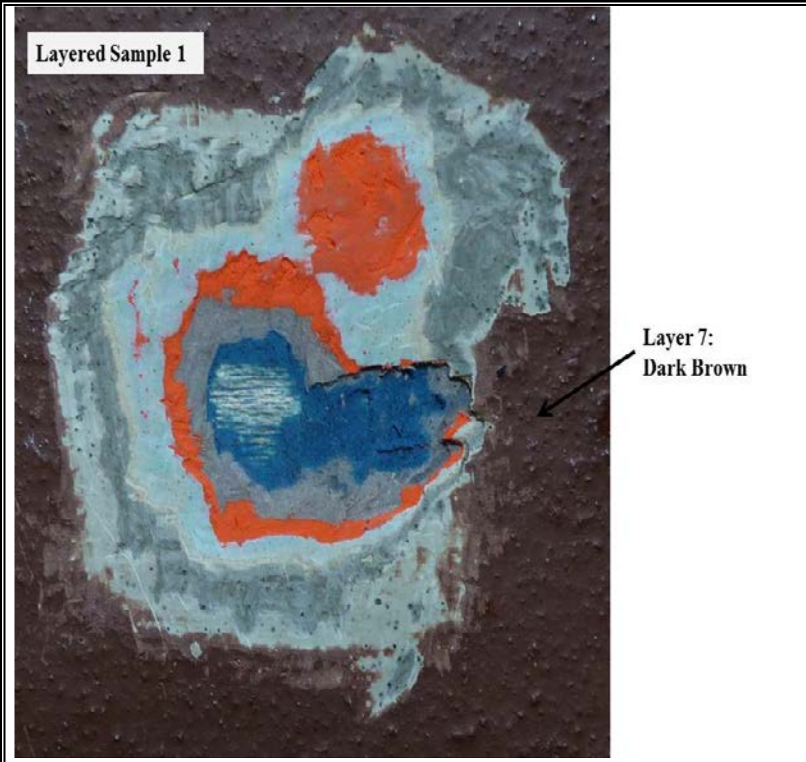
All samples are on wood and pigments are in raw linseed oil

LAYERED SAMPLE 1, Layer 6
Light Ice
PIGMENTS:
small amount of Dark Ice Color (Lead White, Rosin, Verdigris, Lampblack), White Lead
CHEMICAL COMPOUNDS:
$2\ PbCO_3 \cdot Pb(OH)_2$
$C_{15}H_{20}O_6$
$Cu(OH)_2 \cdot (CH_3COO$

Alpha-P & Hyperion Spectrum



C:\Users\User\Desktop\THESIS\Spectra\03.28.13 Bruker Optics AlphaP\diffuse reflectance\EXTRACT_Layered Sample 1 lay 6Fixed.0 Layere		3/29/2013
C:\Users\User\Desktop\THESIS\Spectra\04.11.13 Hyperion Layered Samples\Brown-layered-sample-1.6-ice.0	Brown-sample-ice HYPEI	4/11/2013



Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

LAYERED SAMPLE 1, Layer 7

Dark Brown

PIGMENTS:

Red Ochre, small amount Red Lead, $CaCO_3$

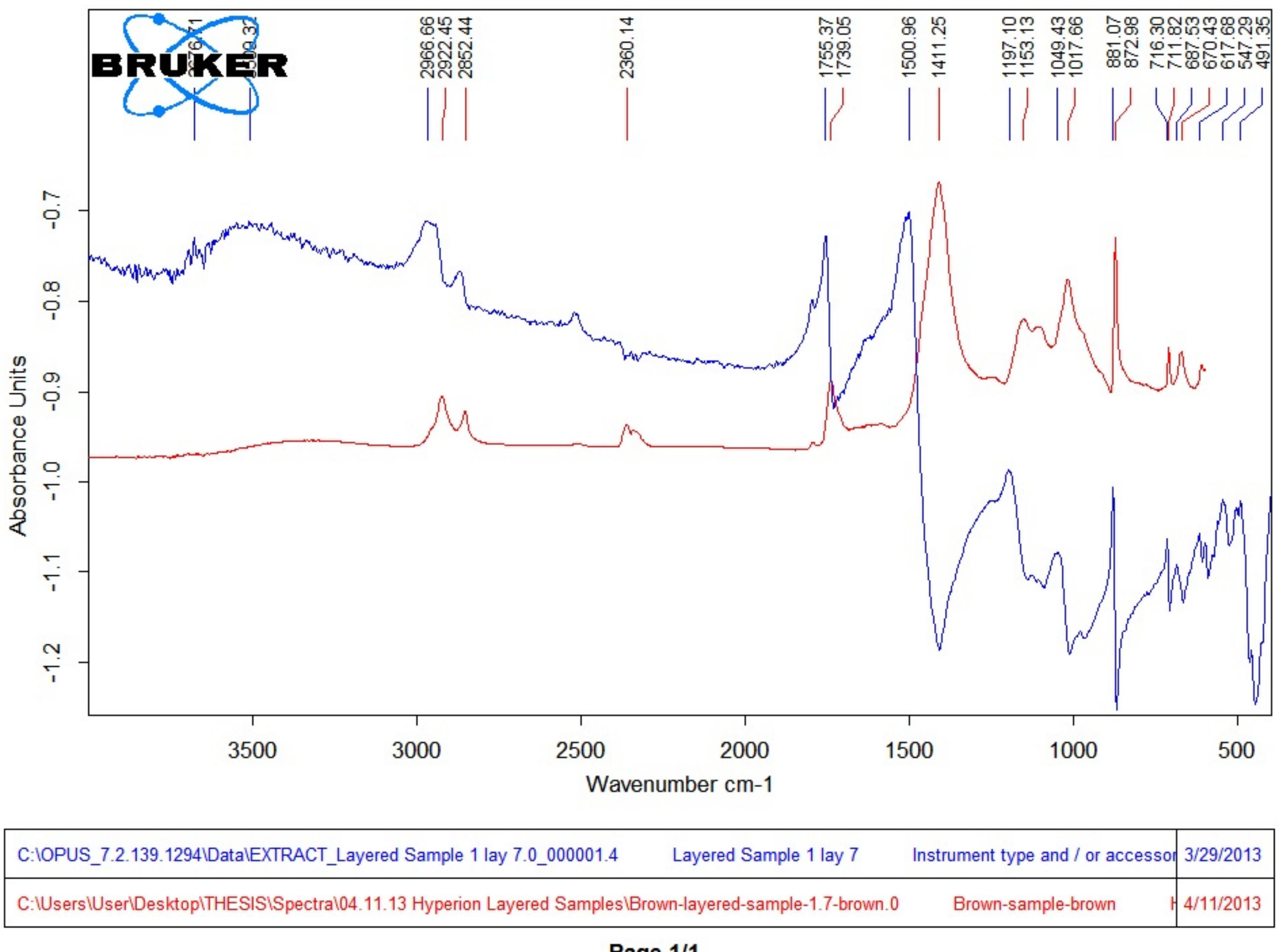
CHEMICAL COMPOUNDS:

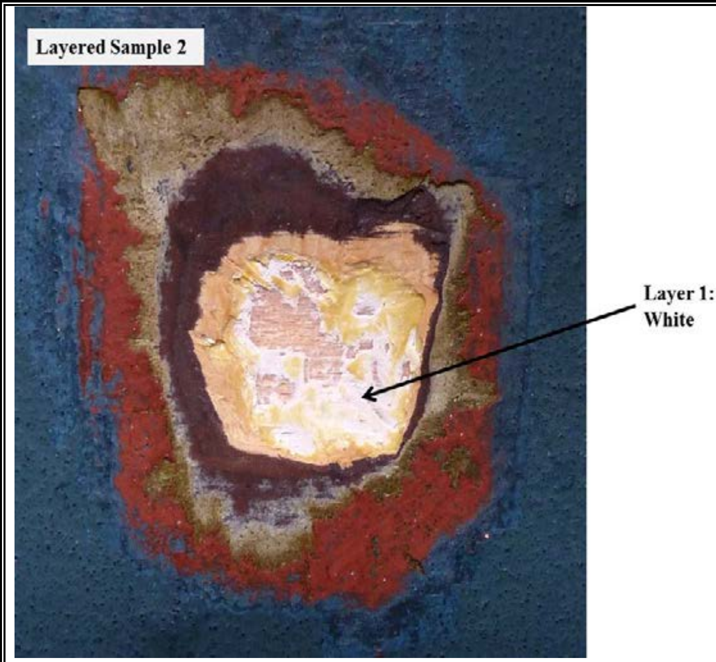
Fe_2O_3

Pb_3O_4

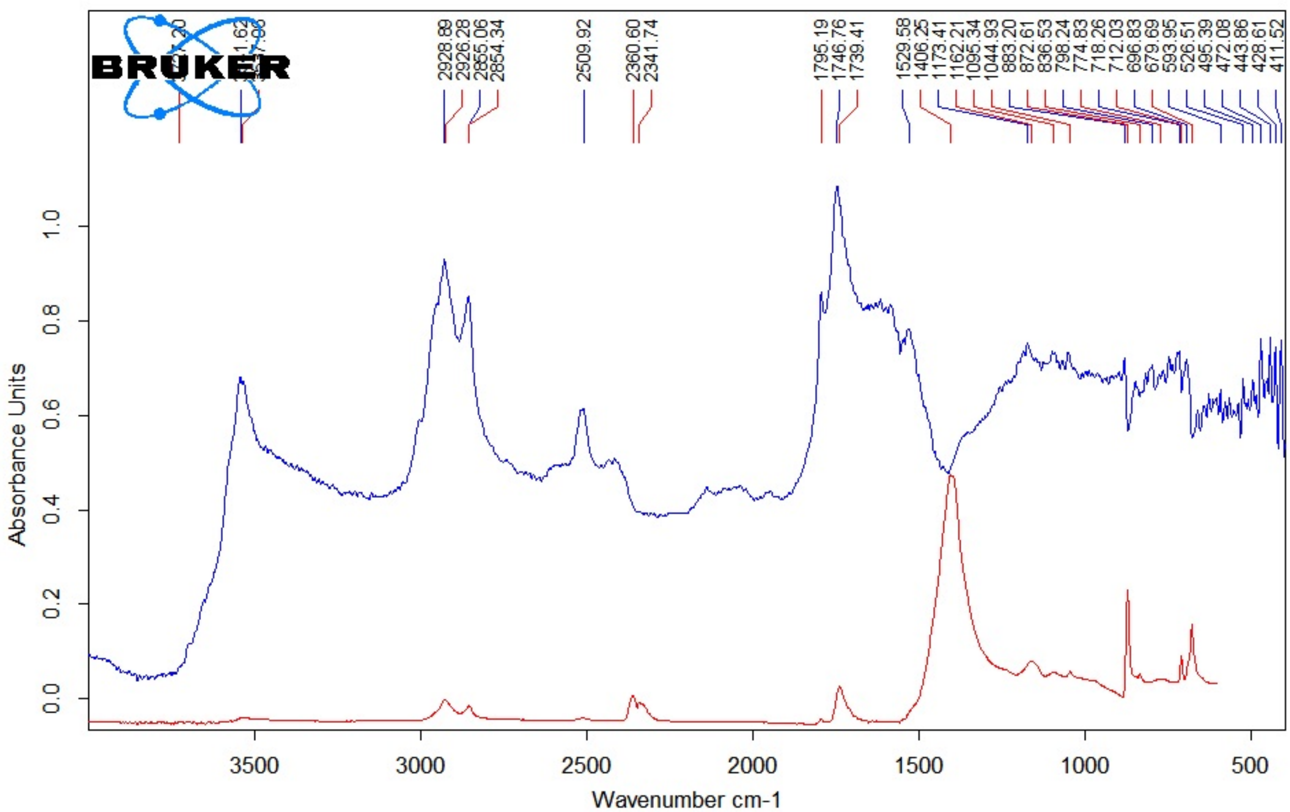
$CaCO_3$

Alpha-P & Hyperion Spectrum



	**Control Sample Data Sheet** All samples are on wood and pigments are in raw linseed oil
	LAYERED SAMPLE 2, Layer 1 White PIGMENTS: Lead White, $CaCO_3$ CHEMICAL COMPOUNDS: $CaCO_3$ $2\,PbCO_3 \cdot Pb(OH)_2$

Alpha-P & Hyperion Spectrum



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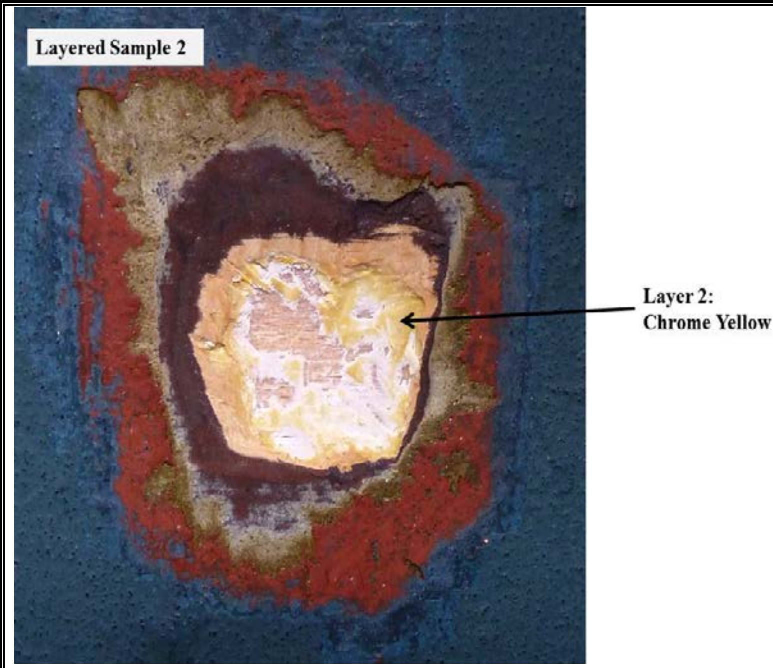
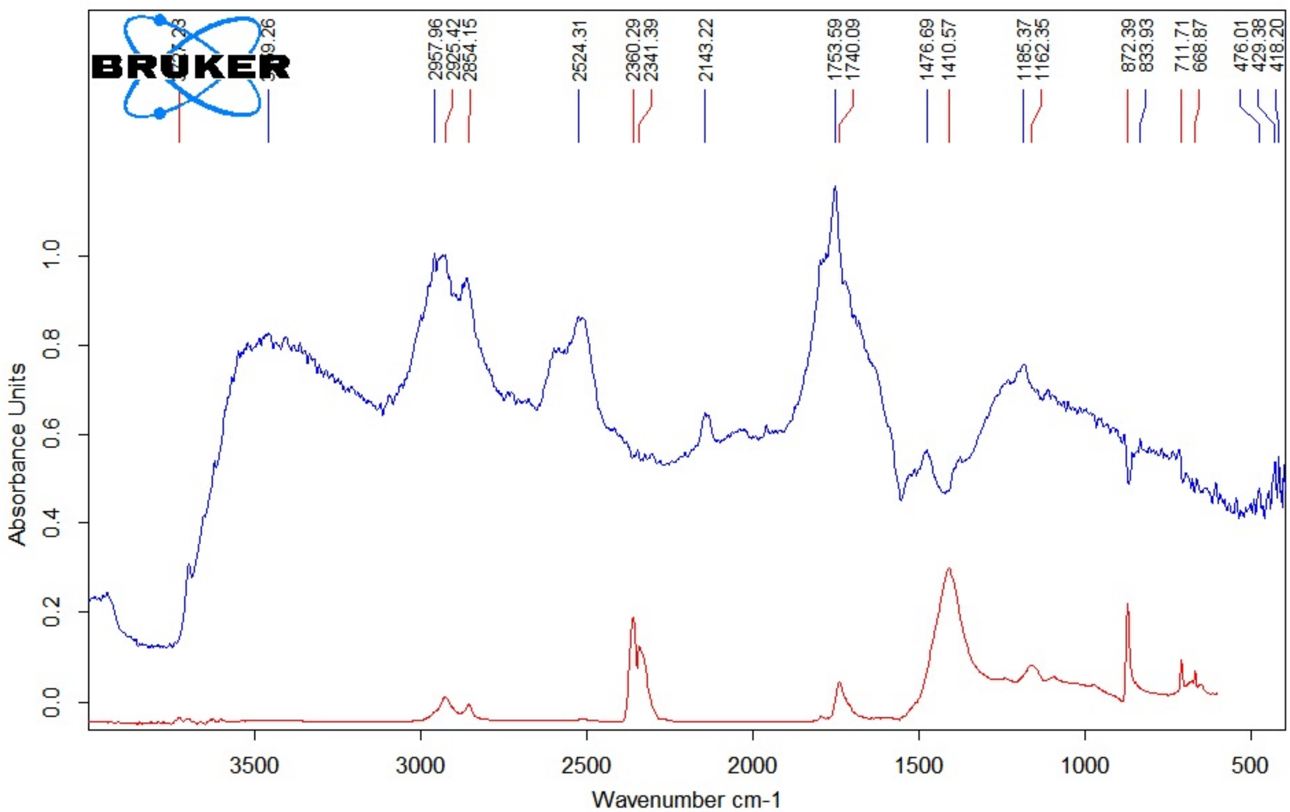


Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

LAYERED SAMPLE 2, Layer 2
Chrome Yellow
PIGMENTS:
Chrome Yellow Deep, $CaCO_3$
CHEMICAL COMPOUNDS:
$PbCrO_4$
$CaCO_3$

Alpha-P & Hyperion Spectrum



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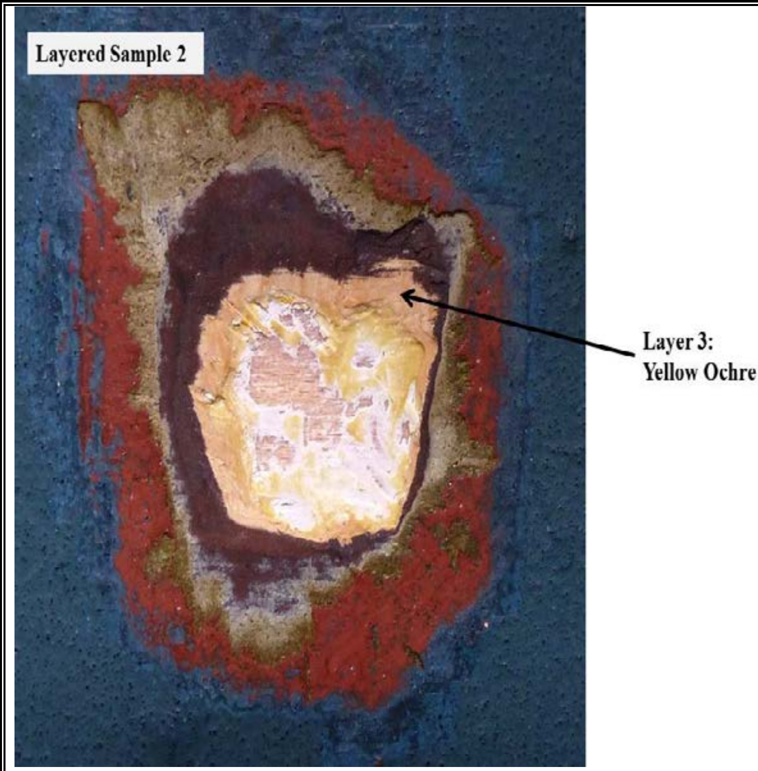
Page 1/1

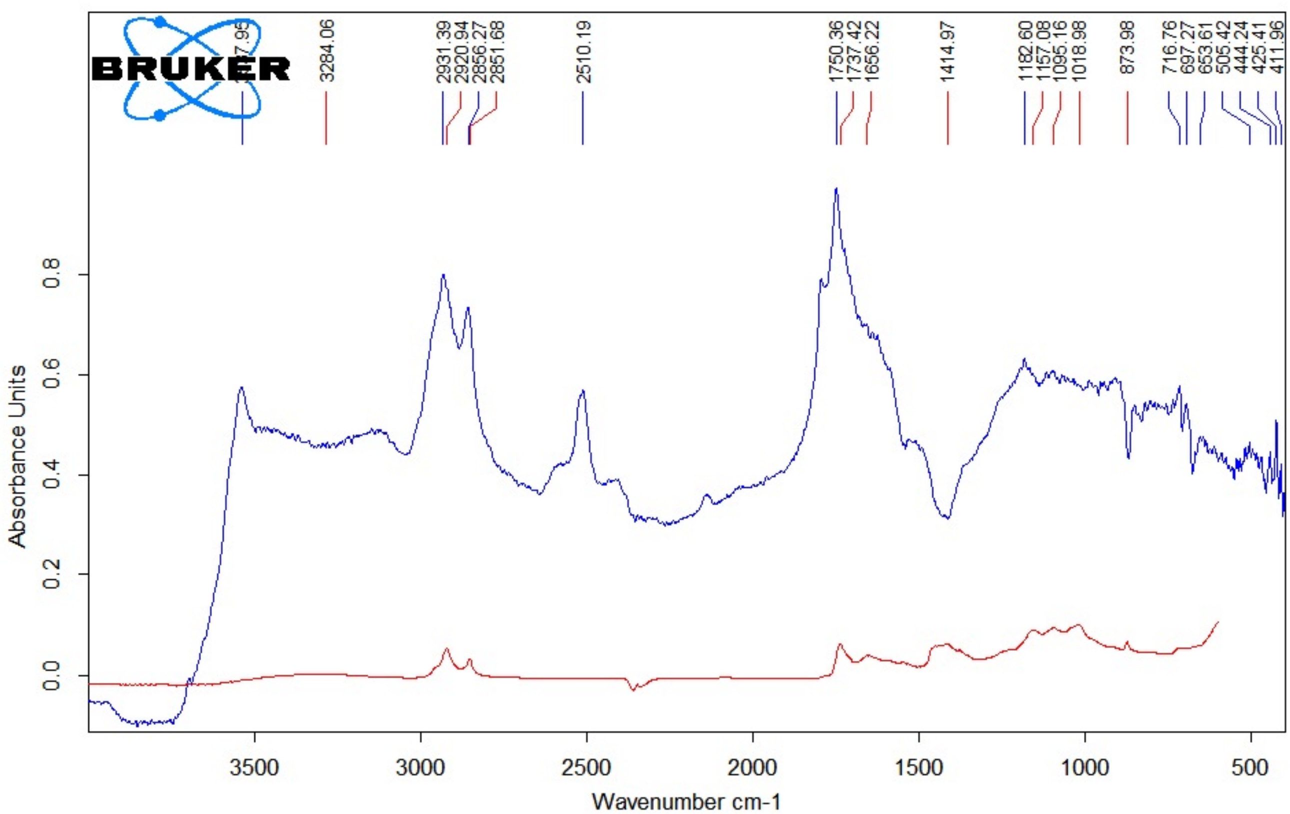


Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

LAYERED SAMPLE 2, Layer 3
Yellow Ochre
PIGMENTS:
Yellow Ochre, Lead White, $CaCO_3$
CHEMICAL COMPOUNDS:
$2\ PbCO_3 \cdot Pb(OH)_2$
FeO(OH))
$CaCO_3$

Alpha-P & Hyperion Spectrum



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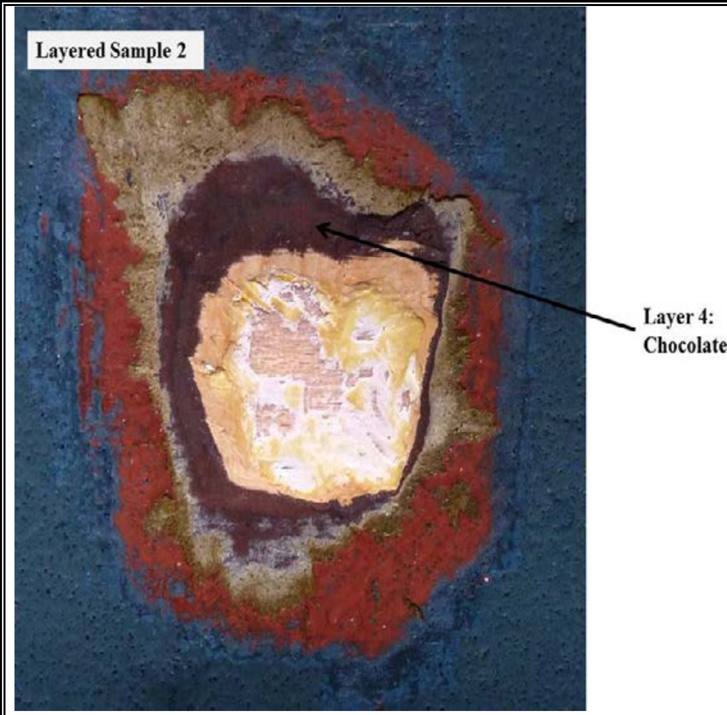


Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

LAYERED SAMPLE 2, Layer 4

Chocolate

PIGMENTS:

Spanish Brown (Caput Mortuum),

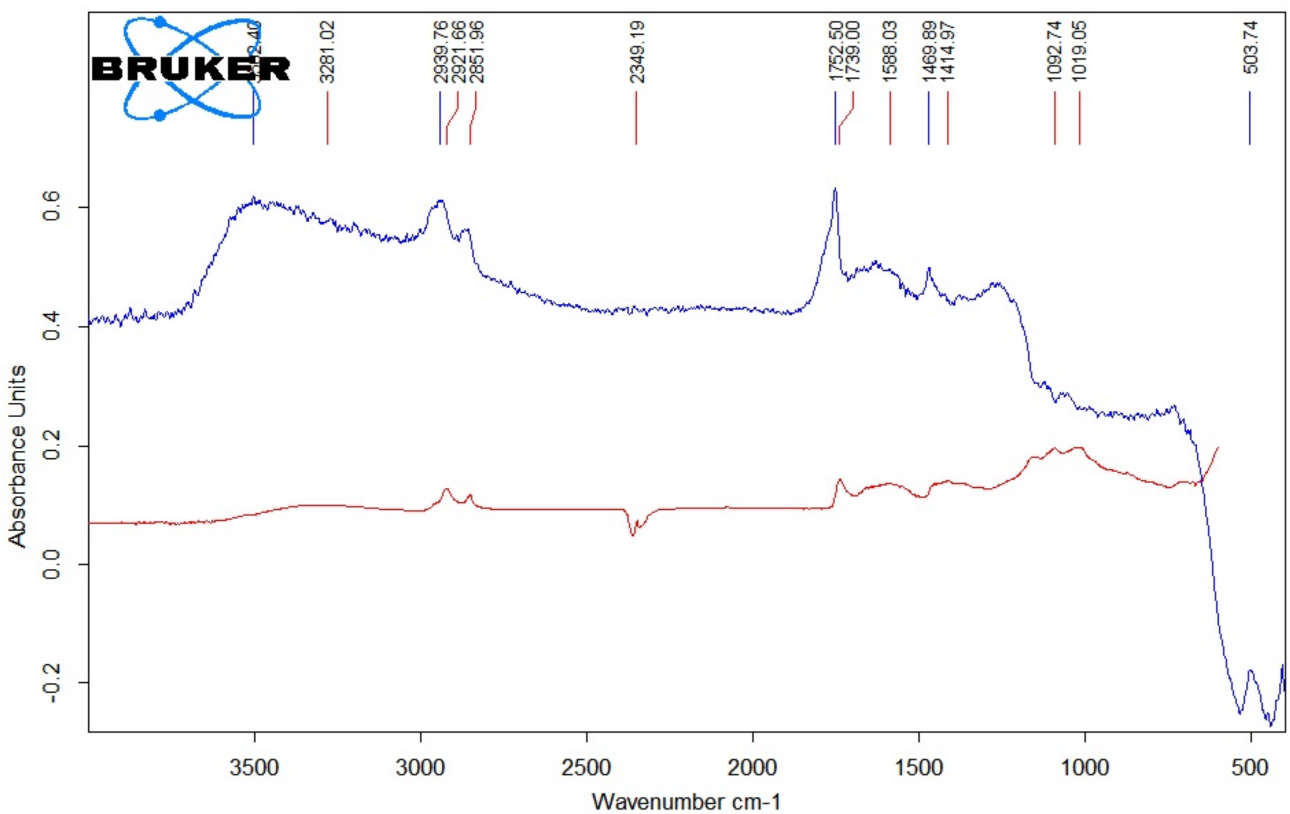
Lampblack

CHEMICAL COMPOUNDS:

Fe_2O_3

C

Alpha-P & Hyperion Spectrum



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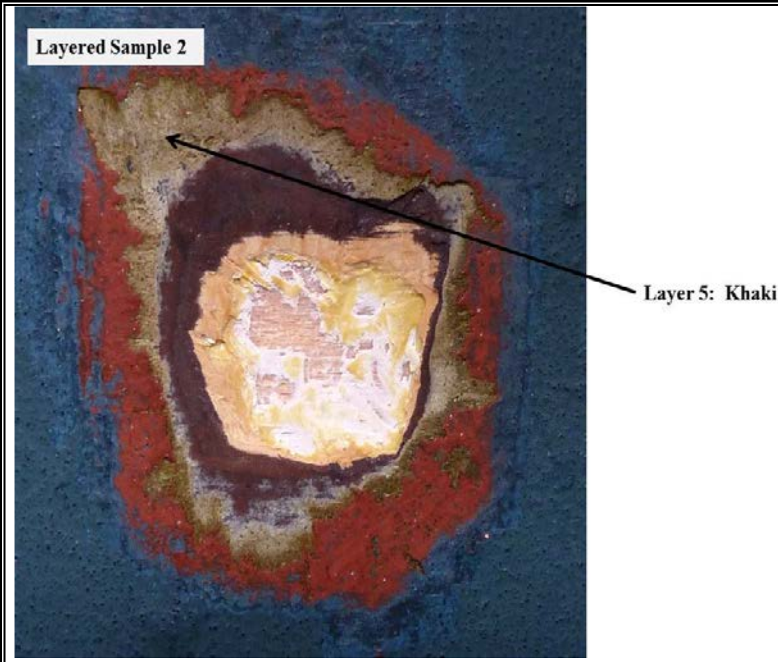
C:\Users\User\Desktop\THESIS\Spectra\04.11.13 Hyperion Layered Samples\Green-layered-sample-2.4-brown.0	Green-sample-brown	H	4/11/2013

Page 1/1



Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

LAYERED SAMPLE 2, Layer 5

PIGMENTS:

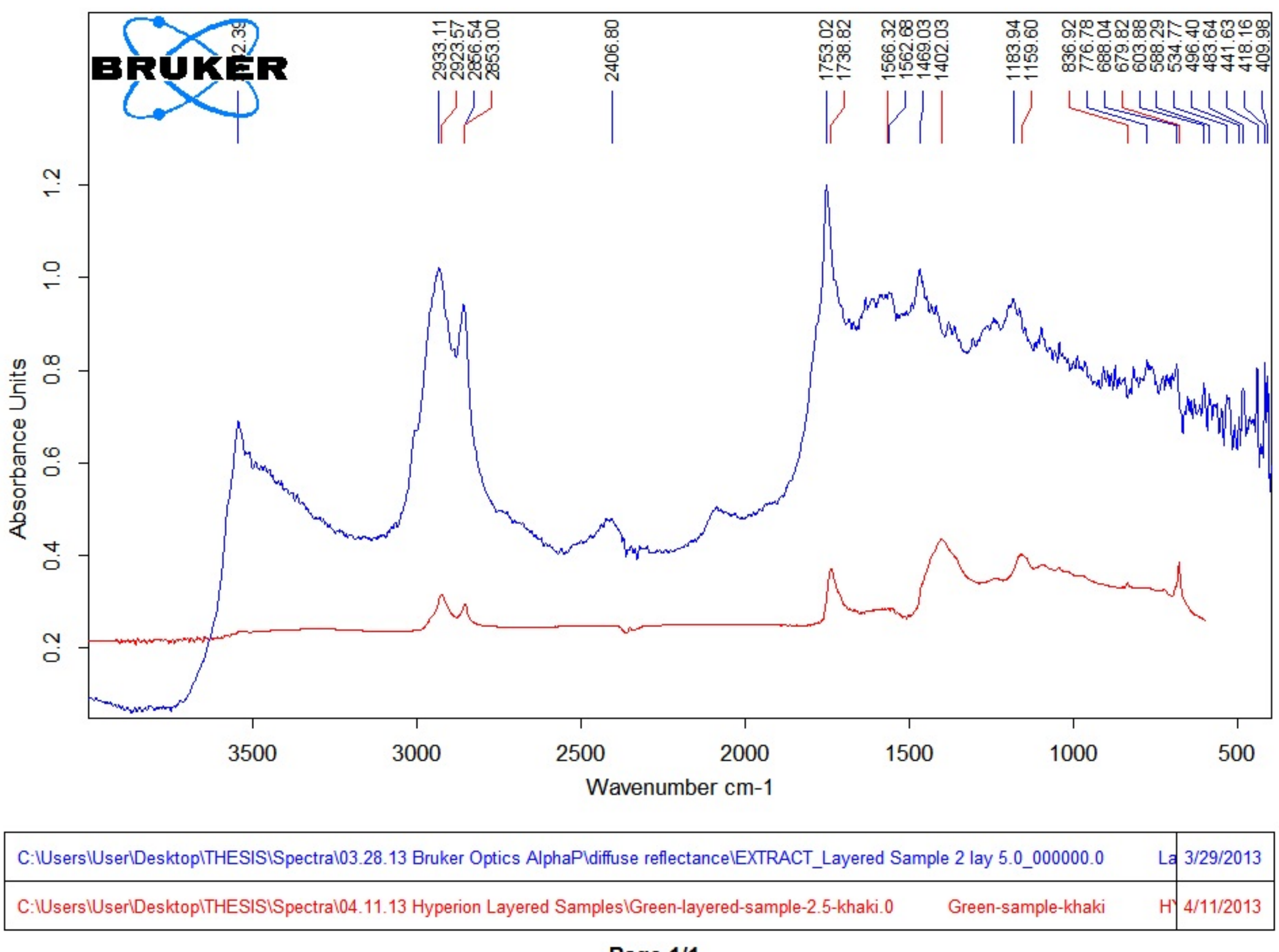
Verdigris, Yellow Ochre, small amount Lead White

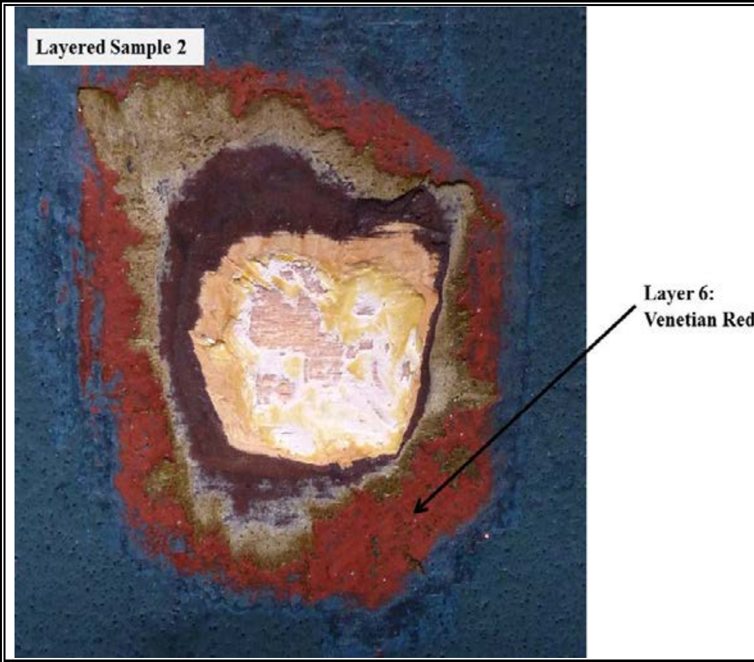
CHEMICAL COMPOUNDS:

$Cu(OH)_2 \cdot (CH_3COO)_2 \cdot 5\ H_2O$

$FeO(OH))$; $2PbCO_3 \cdot Pb(OH)_2$

Alpha-P & Hyperion Spectrum





Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

LAYERED SAMPLE 2, Layer 6

Venetian Red

PIGMENTS:

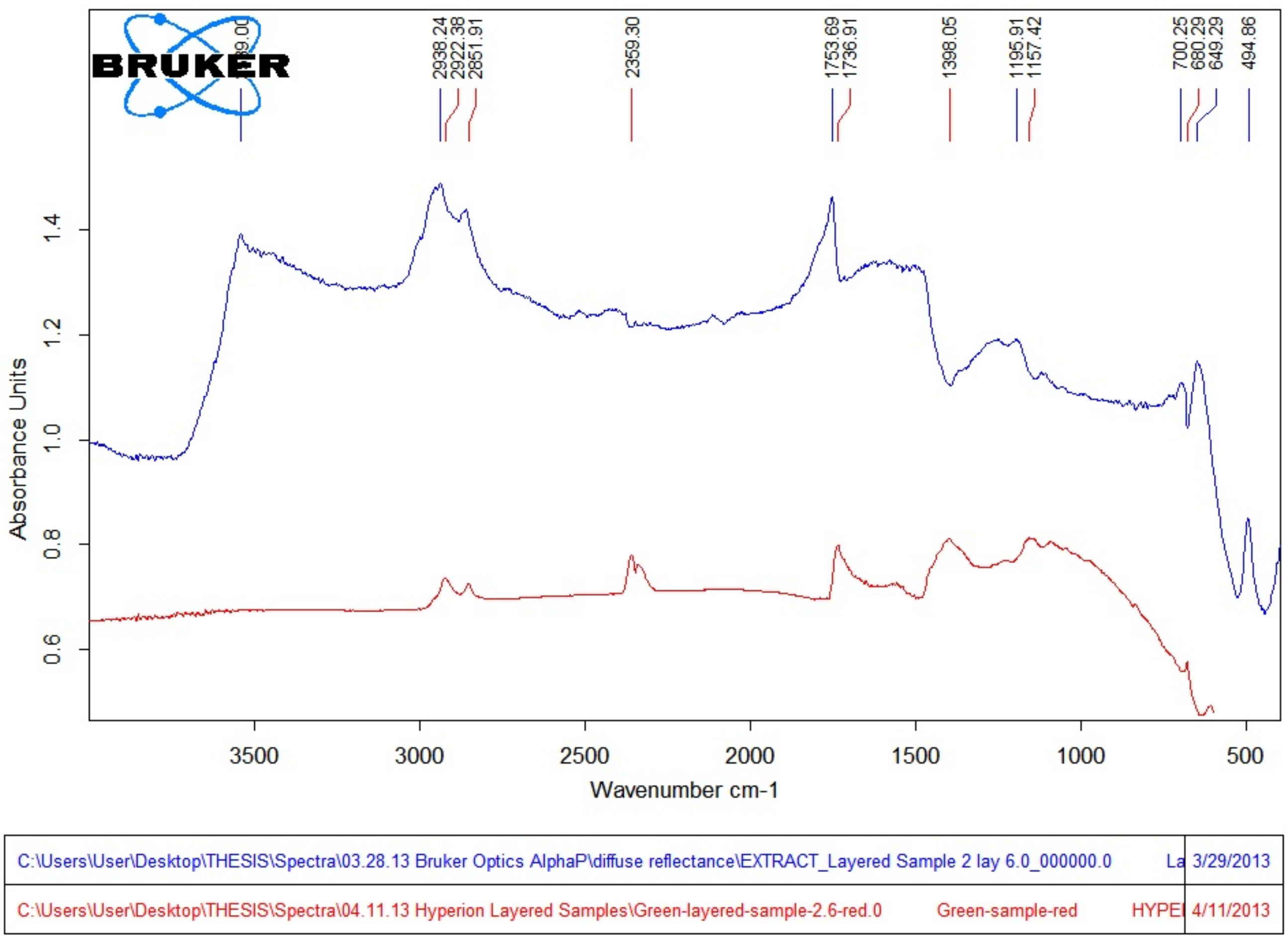
Venetian Lead, Lead White

CHEMICAL COMPOUNDS:

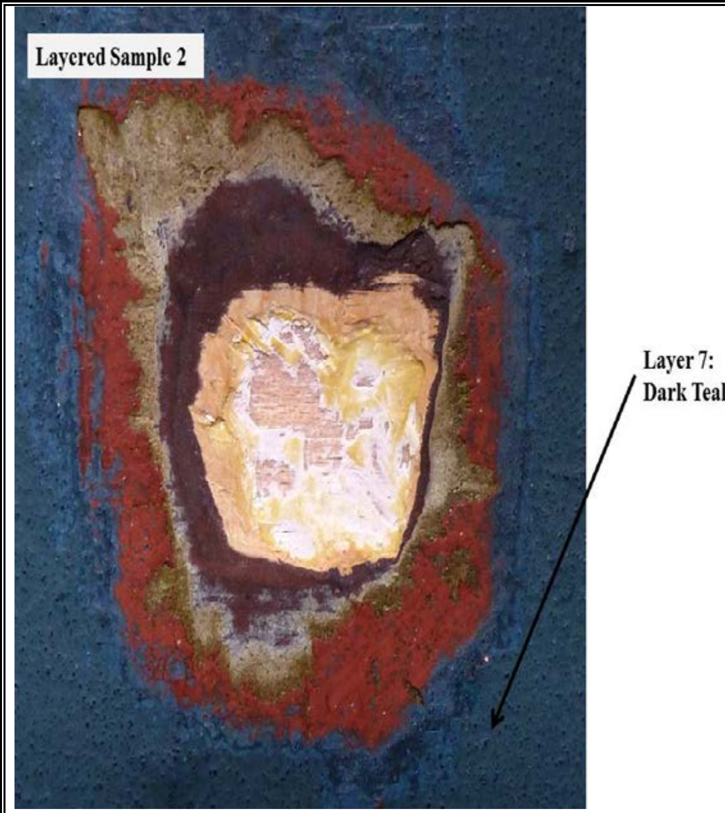
$CaFe_2O_7S$

$2\ PbCO_3 \cdot Pb(OH)_2$

Alpha-P & Hyperion Spectrum



Page 1/1



Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

LAYERED SAMPLE 2, Layer 7

Dark Teal

PIGMENTS:

Prussian Blue, Yellow Ochre, Lead White, $CaCO_3$

CHEMICAL COMPOUNDS:

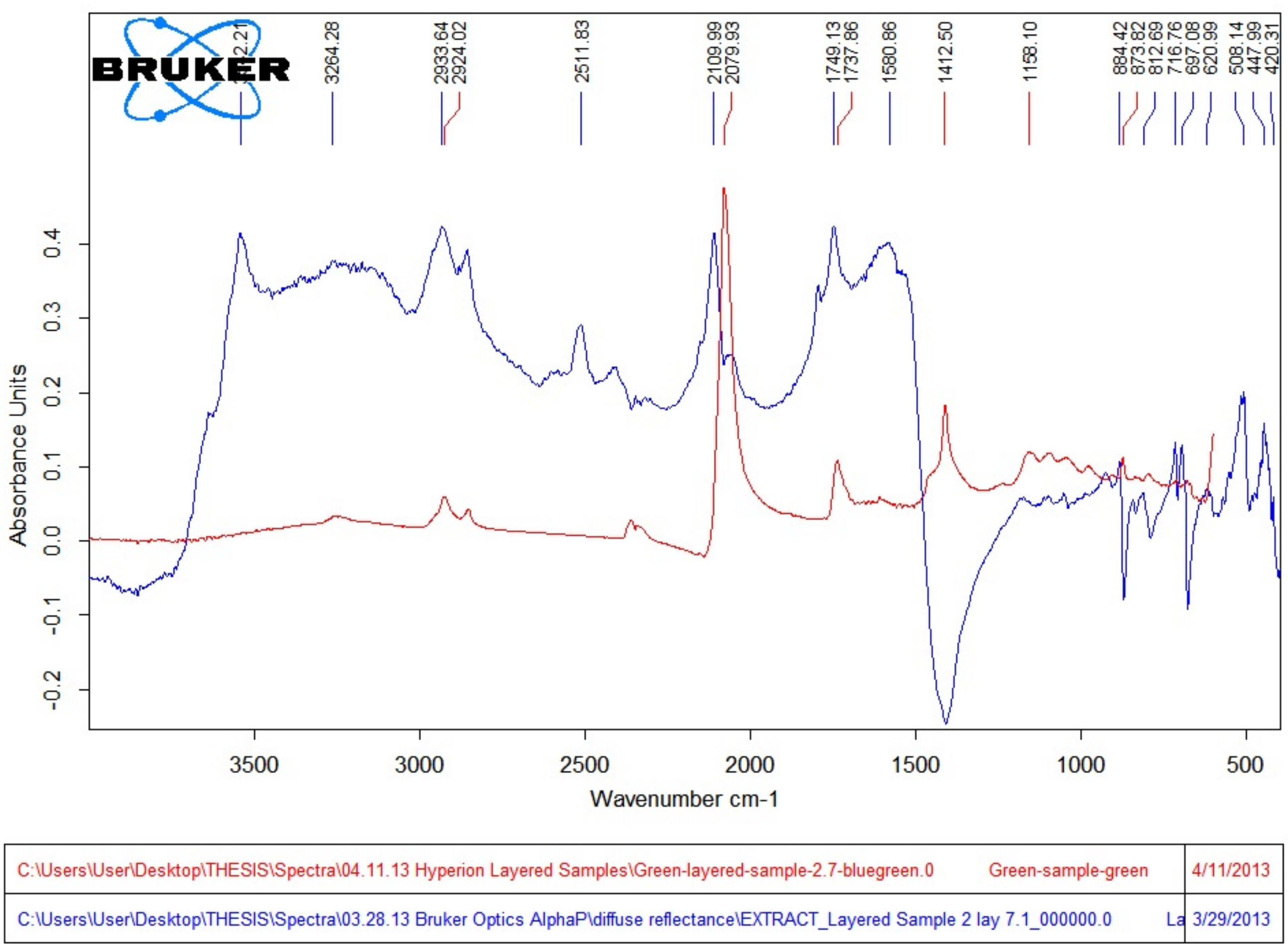
$Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$

Fe_2O_3

$2PbCO_3 \cdot Pb(OH)_2$

$CaCO_3$

Alpha-P & Hyperion Spectrum



Appendix 3: Powder Test Spectra

Sample 17 Powder Test

PIGMENTS:

Spanish Brown (Caput Mortuum), Red Lead, $CaCO_3$

CHEMICAL COMPOUNDS:

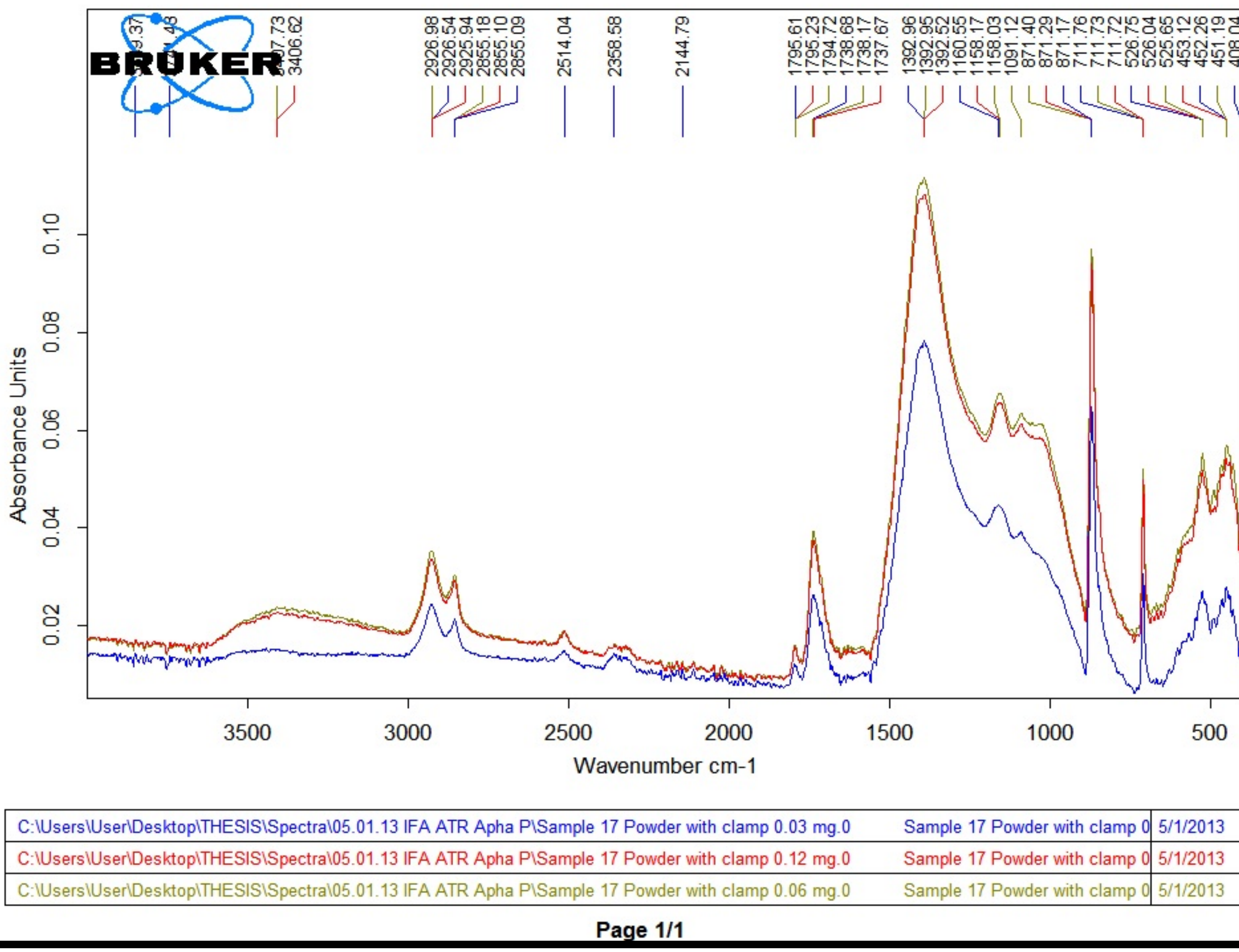
Fe_2O_3

Pb_3O_4

$CaCO_3$

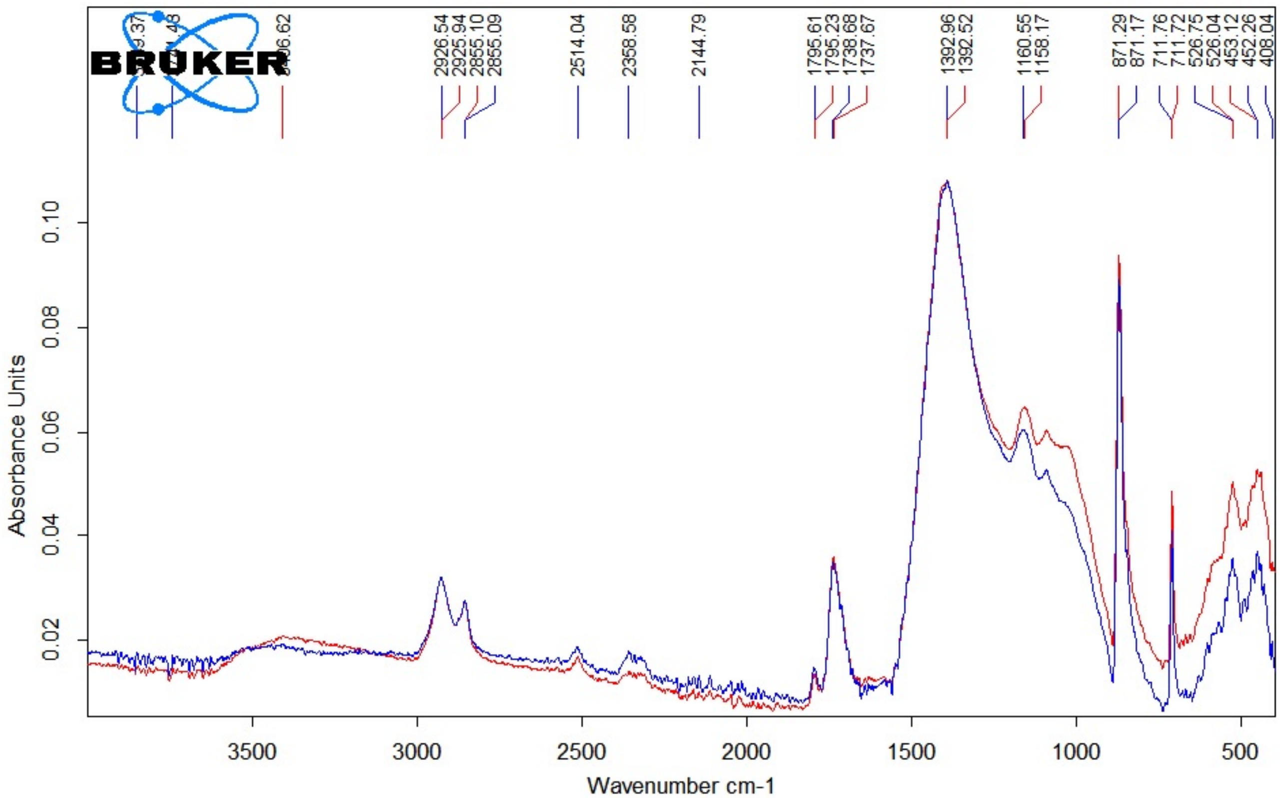
Alpha-P Spectrum from Powder Tests

Powder weights from 0.12 mg to 0.03 mg



Alpha-P Spectrum from Powder Tests: Sample 17

Powder weights 0.12 mg and 0.03 mg (spectra max height)



C:\Users\User\Desktop\THESIS\Spectra\05.01.13 IFA ATR Apha P\Sample 17 Powder with clamp 0.03 mg.0	Sample 17 Powder with clamp 0	5/1/2013
C:\Users\User\Desktop\THESIS\Spectra\05.01.13 IFA ATR Apha P\Sample 17 Powder with clamp 0.12 mg.0	Sample 17 Powder with clamp 0	5/1/2013

Sample 22 Powder Test

PIGMENTS:

Lead White, Verdigris

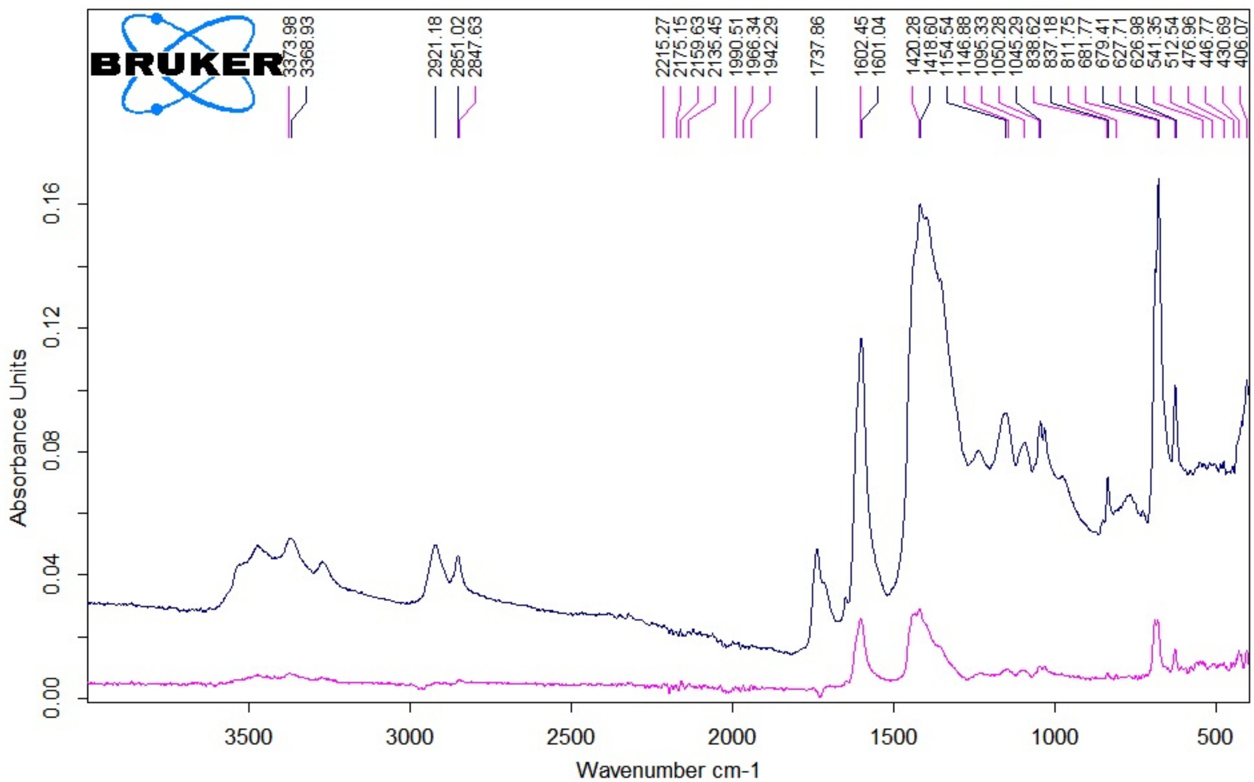
CHEMICAL COMPOUNDS:

$2\ PbCO_3 \cdot Pb(OH)_2$

$Cu(OH)_2 \cdot (CH_3COO)_2 \cdot 5\ H_2O$

Alpha-P Spectrum from Powder Tests

Clamp vs. without clamp



C:\Users\User\Desktop\THESIS\Spectra\05.01.13 IFA ATR Apha P\Sample 22 Powder.0	Sample 22 Powder	Instrument type and / or ac	5/1/2013
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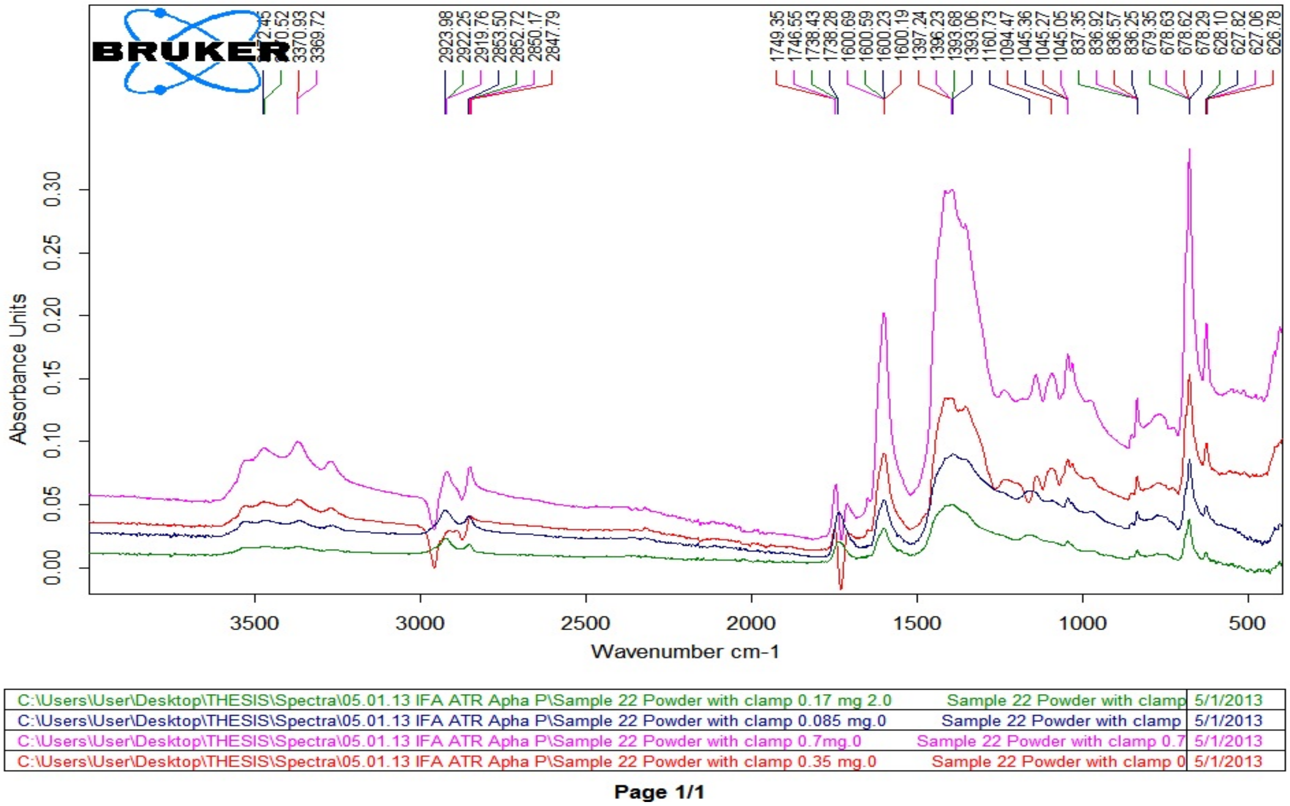
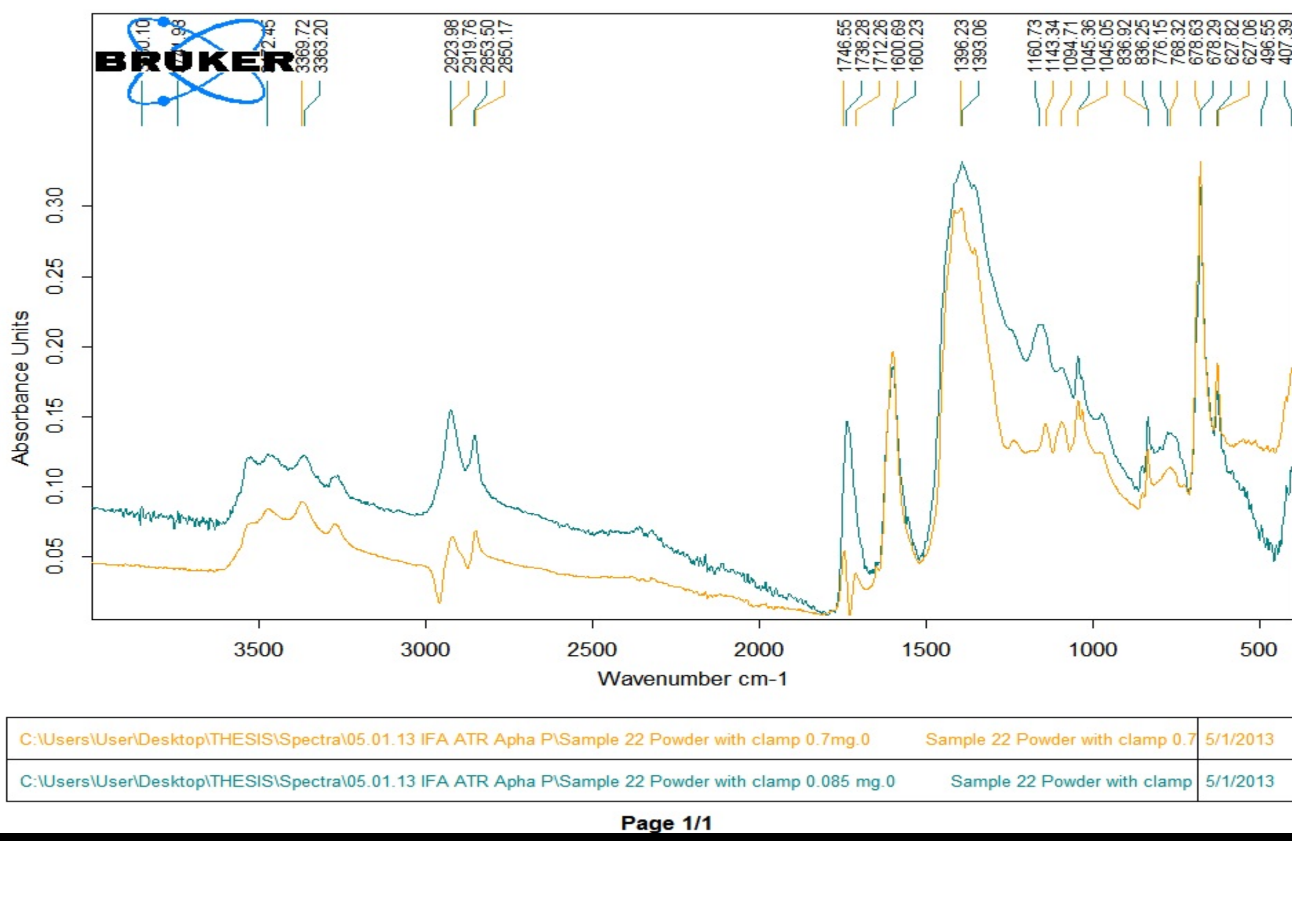
Alpha-P Spectrum from Powder Tests: Sample 22

Powder weights from 0.7 mg to 0.085 mg



Powder weights 0.7 mg and 0.085 mg (spectra max height)



Appendix 4: Paint Chip Test Spectra

Sample 22 Paint Chip Test

PIGMENTS:

Lead White, Verdigris

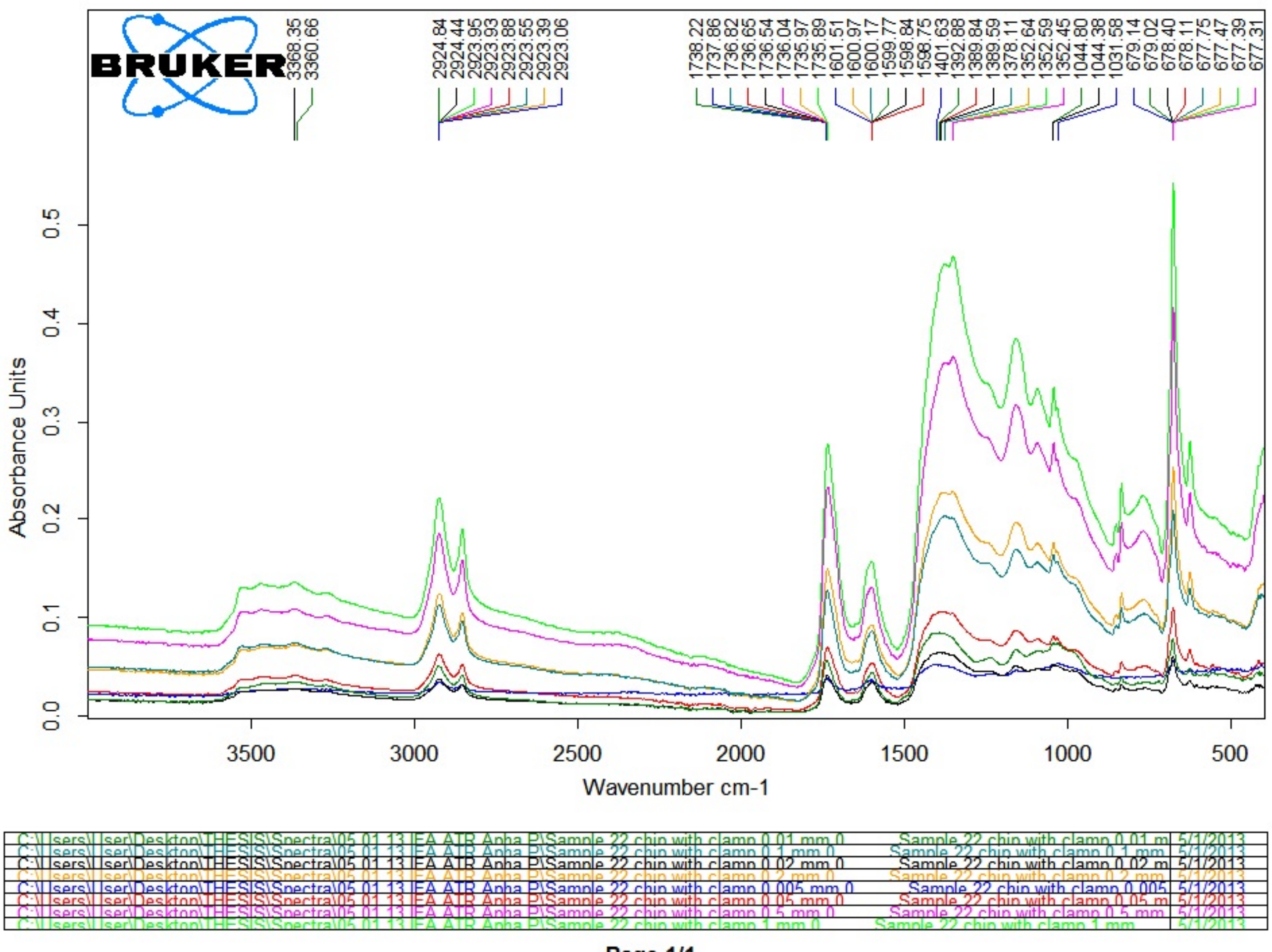
CHEMICAL COMPOUNDS:

$2\ PbCO_3 \cdot Pb(OH)_2$

$Cu(OH)_2\ \cdot (CH_3COO)_2\ \cdot 5\ H_2O$

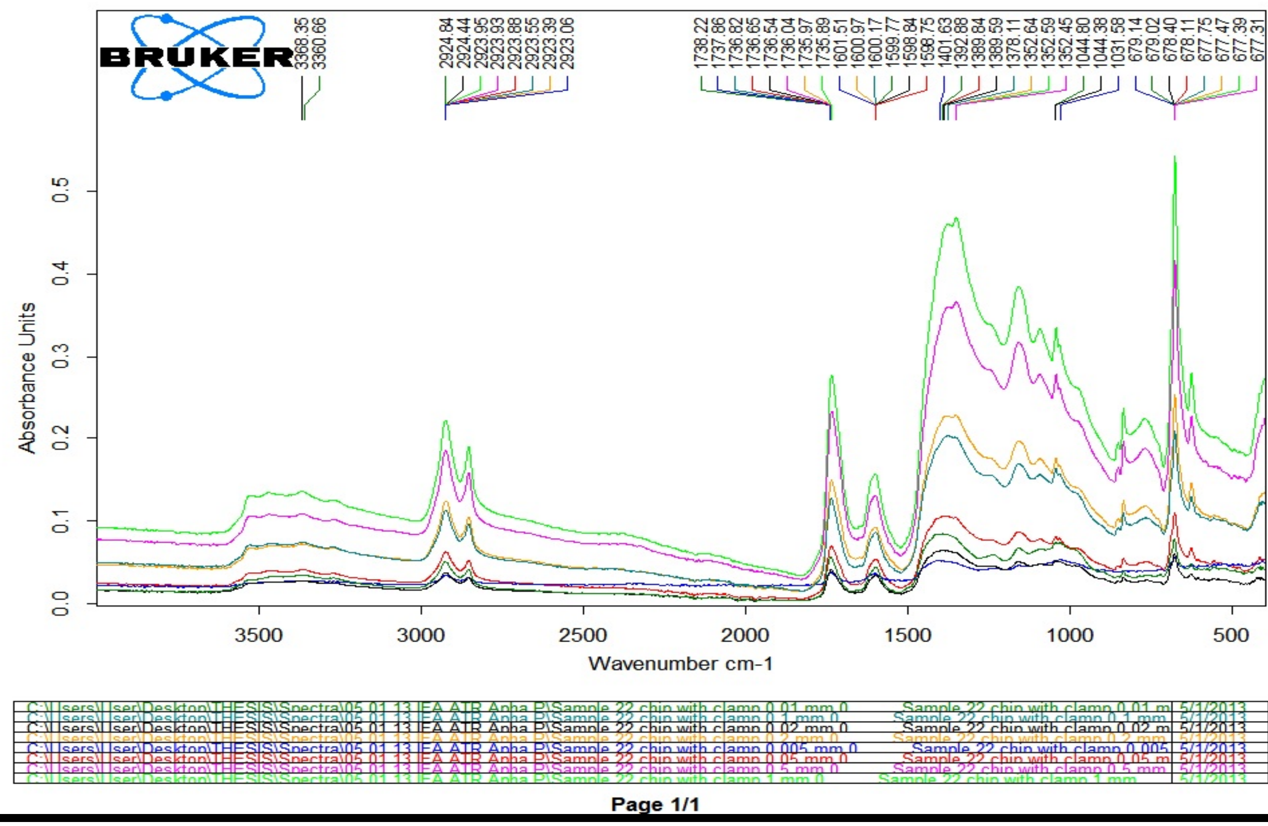
Alpha-P Spectrum from Paint Chips Tests

Paint chips from 1.0 mm to 0.005 mm

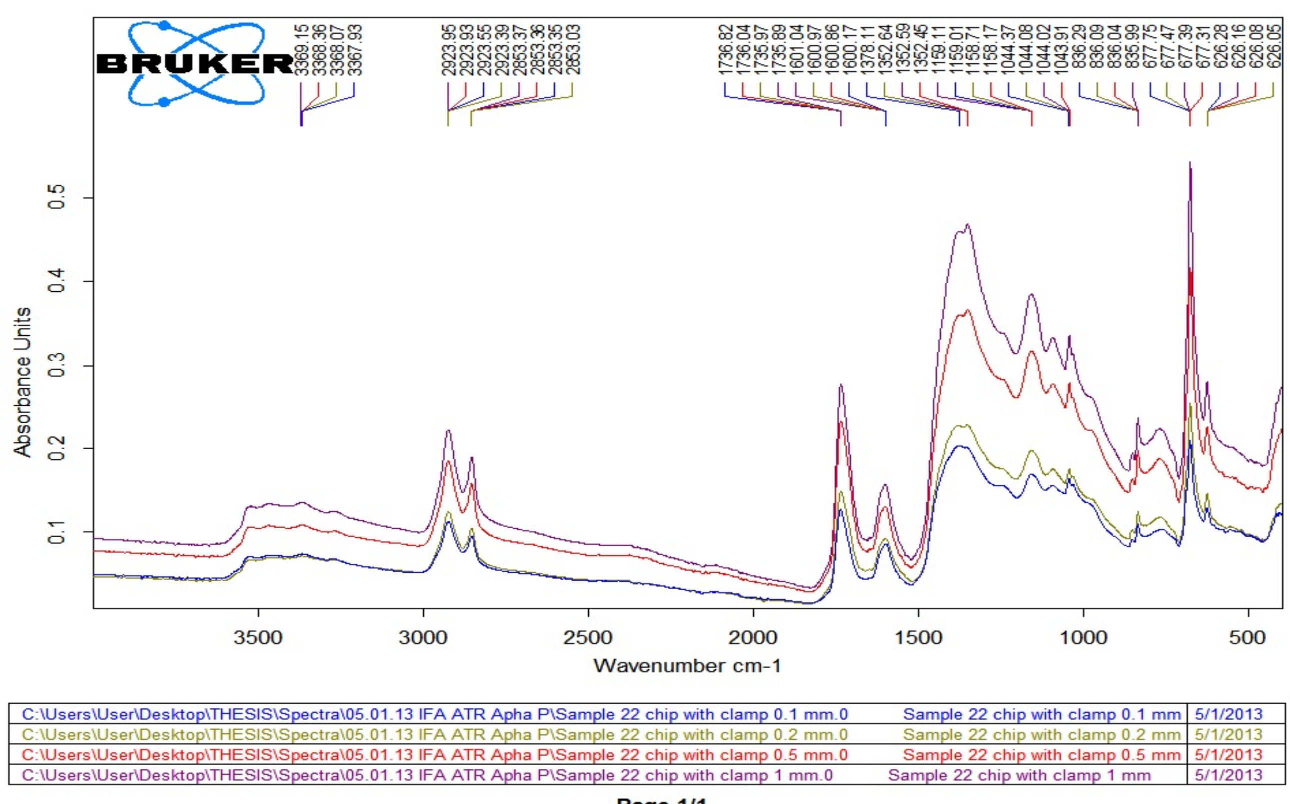


Alpha-P Spectrum from Powder Tests: Sample 22

Paint chips from 1.0 mm to 0.005 mm

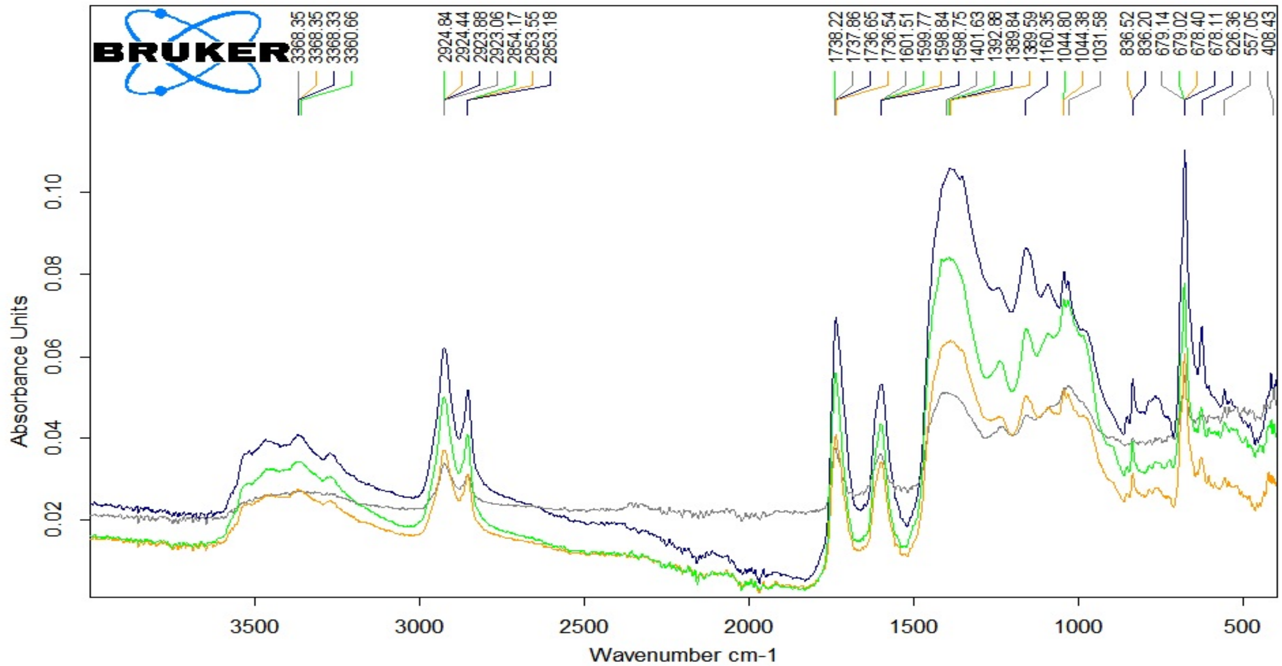


Paint chips from 1.0 mm to 0.1 mm



Alpha-P Spectrum from Powder Tests: Sample 22

Paint chips from 0.05 mm to 0.005 mm



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C:\Users\User\Desktop\THESIS\Spectra\05.01.13 IFA ATR Apha P\Sample 22 chip with clamp 0.02 mm.0	Sample 22 chip with clamp 0.02 m	5/1/2013
C:\Users\User\Desktop\THESIS\Spectra\05.01.13 IFA ATR Apha P\Sample 22 chip with clamp 0.005 mm.0	Sample 22 chip with clamp 0.005	5/1/2013
C:\Users\User\Desktop\THESIS\Spectra\05.01.13 IFA ATR Apha P\Sample 22 chip with clamp 0.05 mm.0	Sample 22 chip with clamp 0.05 m	5/1/2013

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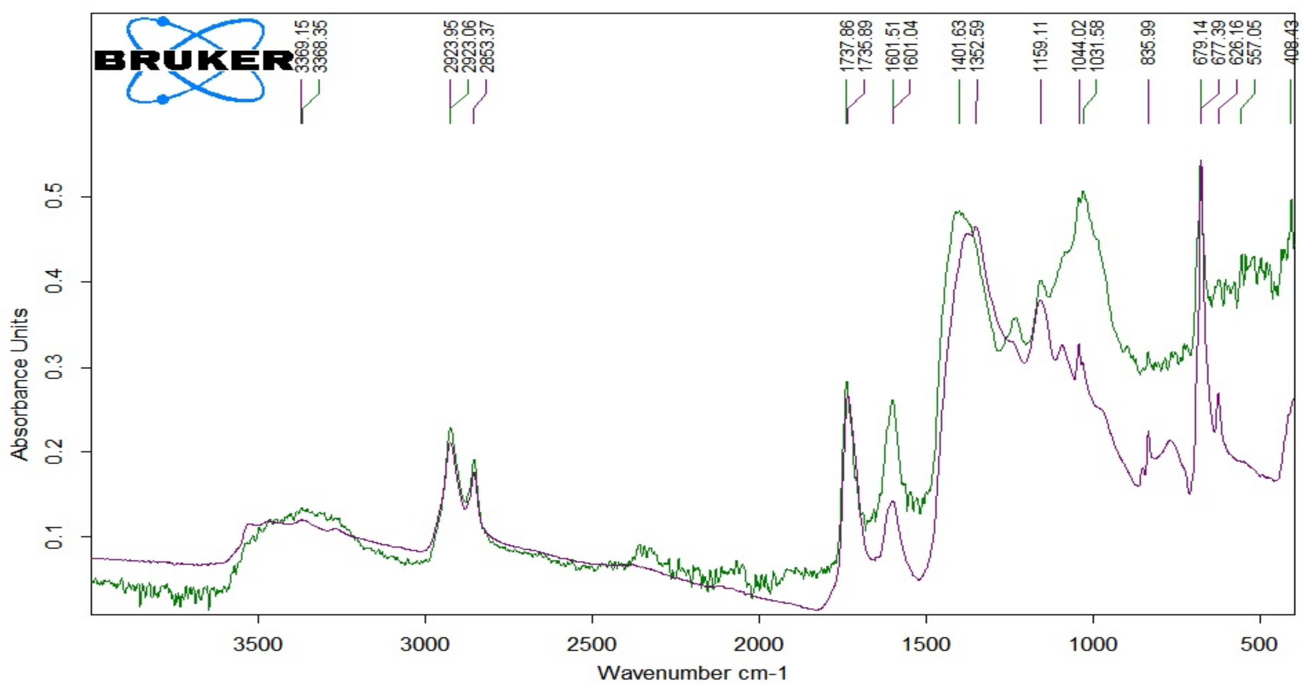
Paint chips 1.0 mm and 0.005 mm (spectra max height)



C:\Users\User\Desktop\THESIS\Spectra\05.01.13 IFA ATR Apha P\Sample 22 chip with clamp 1 mm.0	Sample 22 chip with clamp 1 mm	5/1/2013
C:\Users\User\Desktop\THESIS\Spectra\05.01.13 IFA ATR Apha P\Sample 22 chip with clamp 0.005 mm.0	Sample 22 chip with clamp 0.005	5/1/2013

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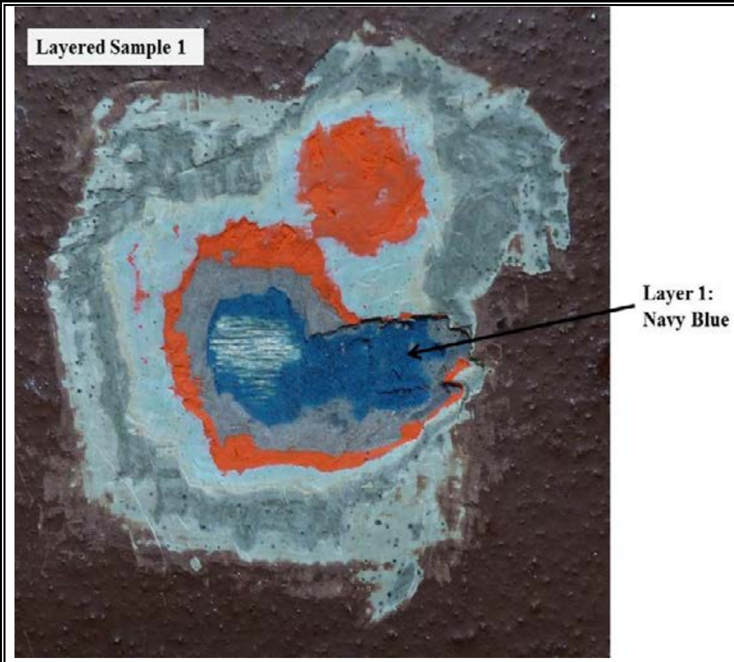
Appendix 5: Alpha-P DRIFTS Spectra vs. ATR Spectra



Alpha-P DRIFTS vs. ATR Spectra

All samples are on wood and pigments are in raw linseed oil

Layered Sample 1 Layer 1 vs. Sample 8

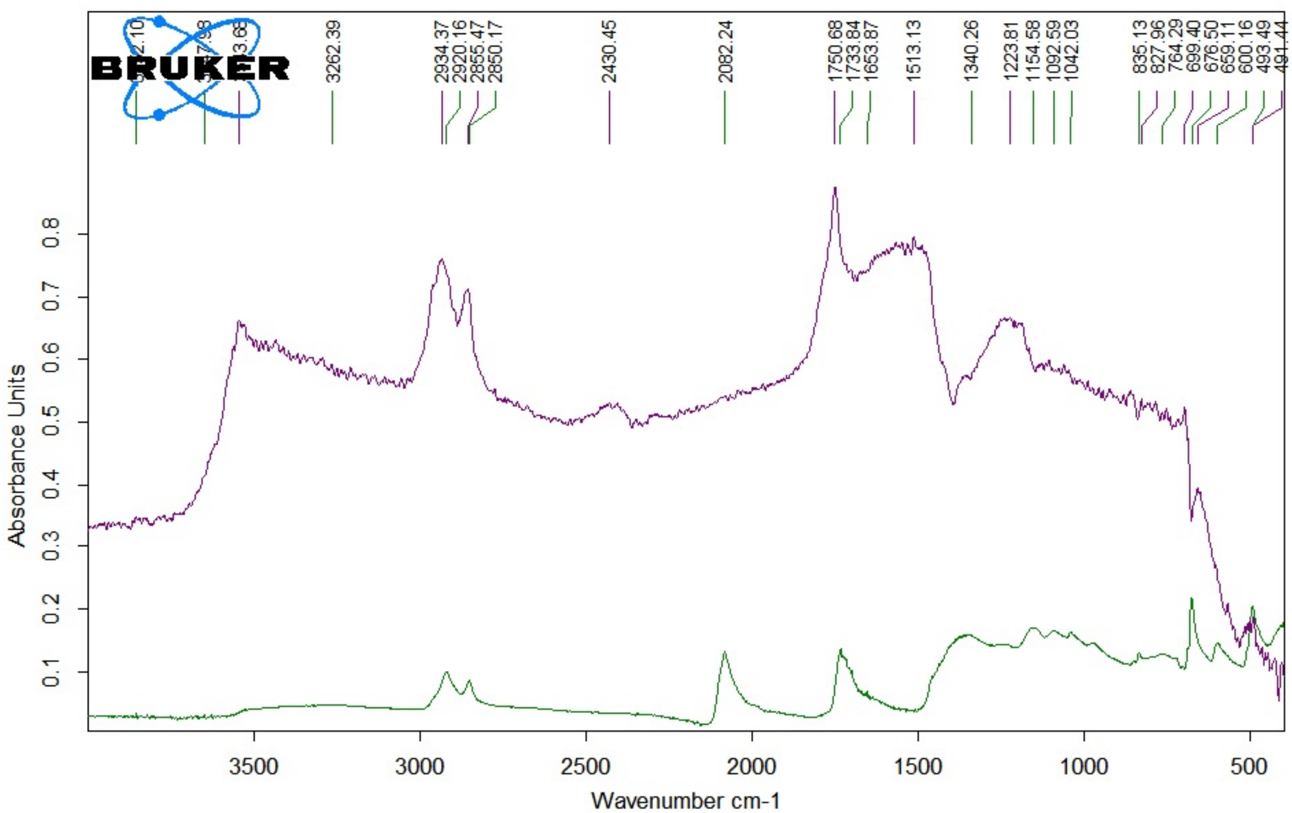
PIGMENTS:

Prussian Blue & Lead White

CHEMICAL COMPOUNDS:

$Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$

$2PbCO_3 \cdot Pb(OH)_2$



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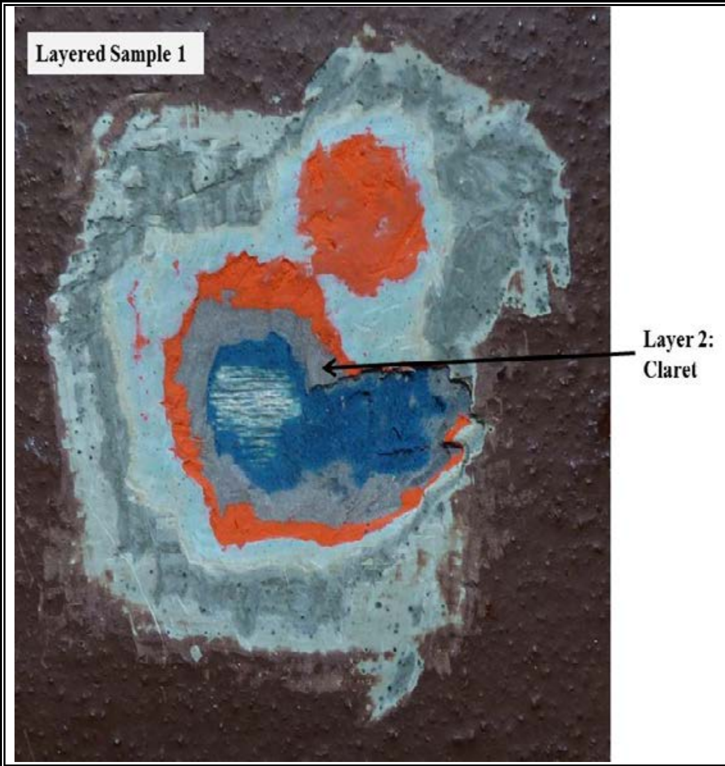


Alpha-P DRIFTS vs. ATR Spectra

All samples are on wood and pigments are in raw linseed oil

Layered Sample 1, Layer 2 vs. Sample 13

PIGMENTS:

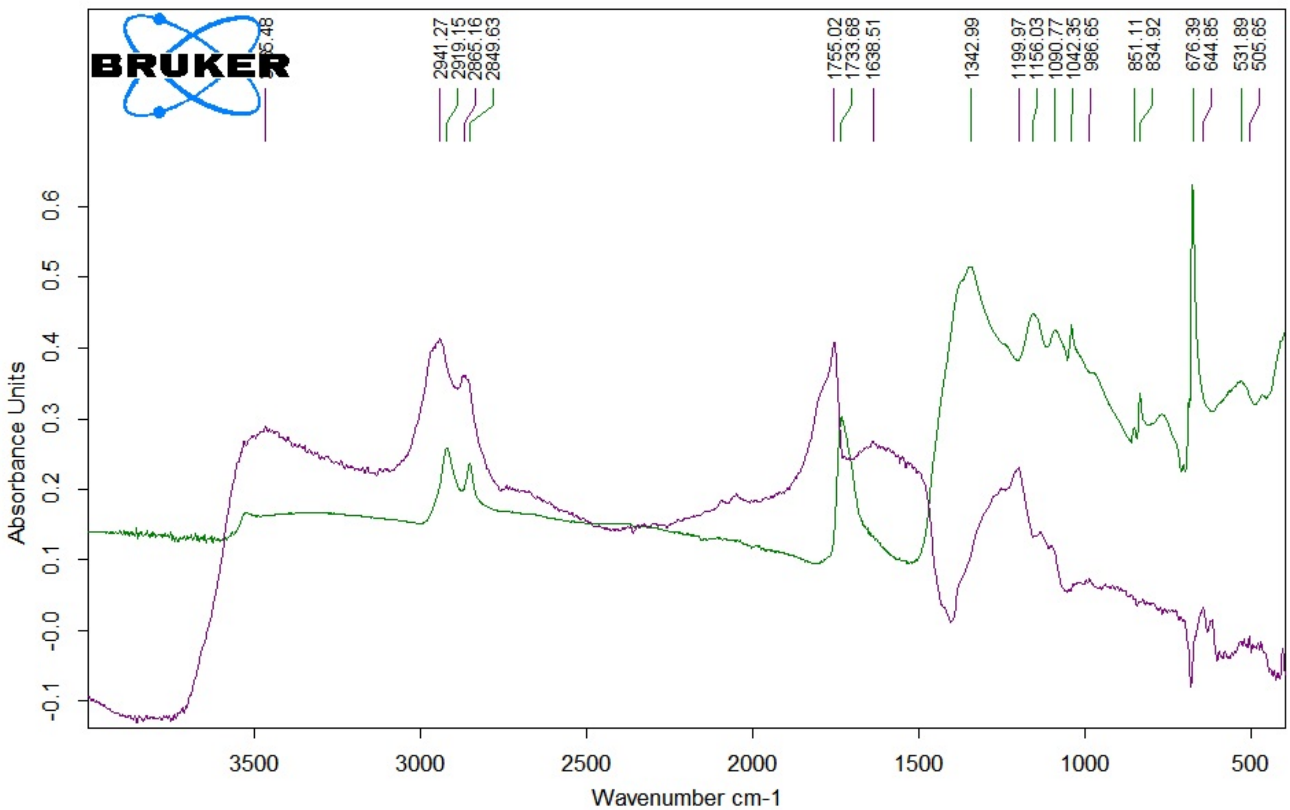
White Lead, Spanish Brown (Caput Mortuum), Lampblack

CHEMICAL COMPOUNDS:

$2\ PbCO_3 \cdot Pb(OH)_2$

Fe_2O_3

C



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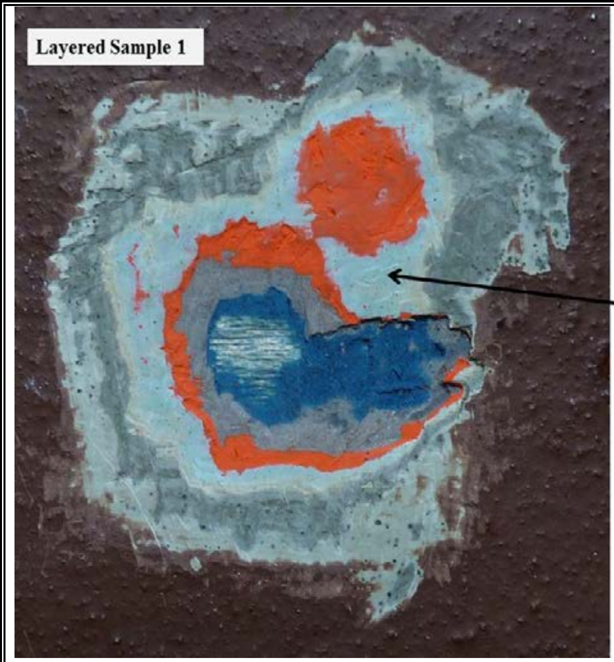


Alpha-P DRIFTS vs. ATR Spectra

All samples are on wood and pigments are in raw linseed oil

Layered Sample 1, Layer 4 vs. Sample 7

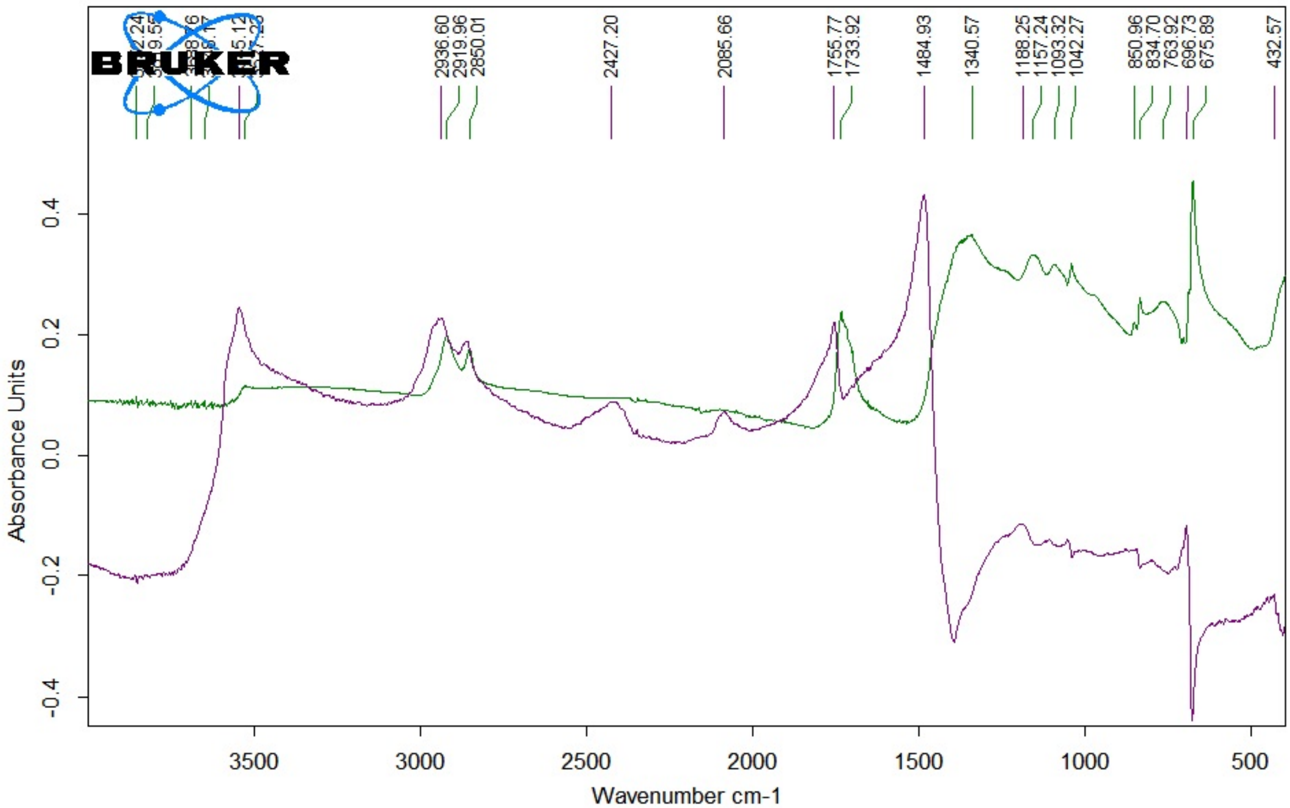
PIGMENTS:

Prussian Blue, Lead White

CHEMICAL COMPOUNDS:

$Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$

$2PbCO_3 \cdot Pb(OH)_2$



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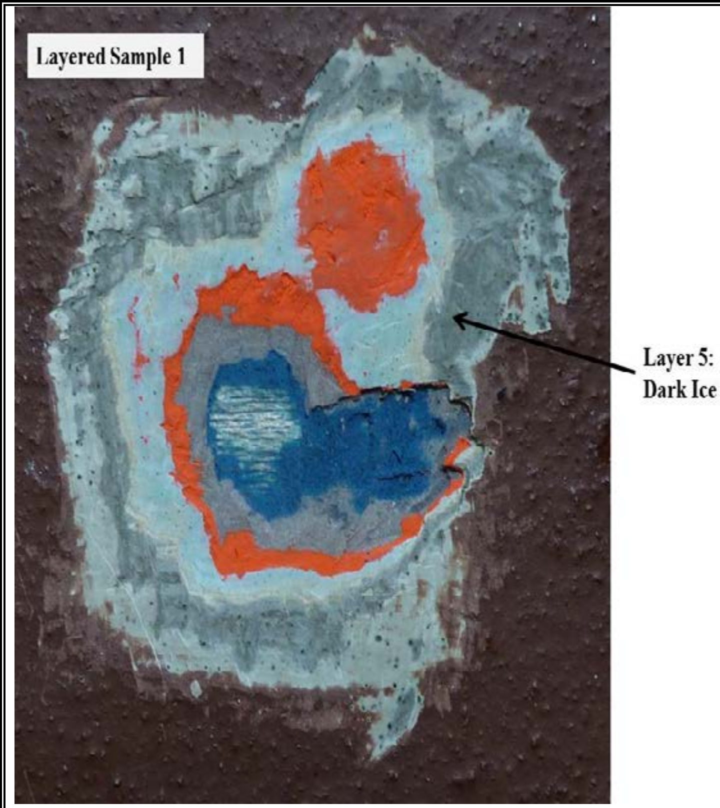


Alpha-P DRIFTS vs. ATR Spectra

All samples are on wood and pigments are in raw linseed oil

Layered Sample 1 Layer 5 vs. Sample 12

PIGMENTS:

Lead White, Rosin, Verdigris, Lampblack

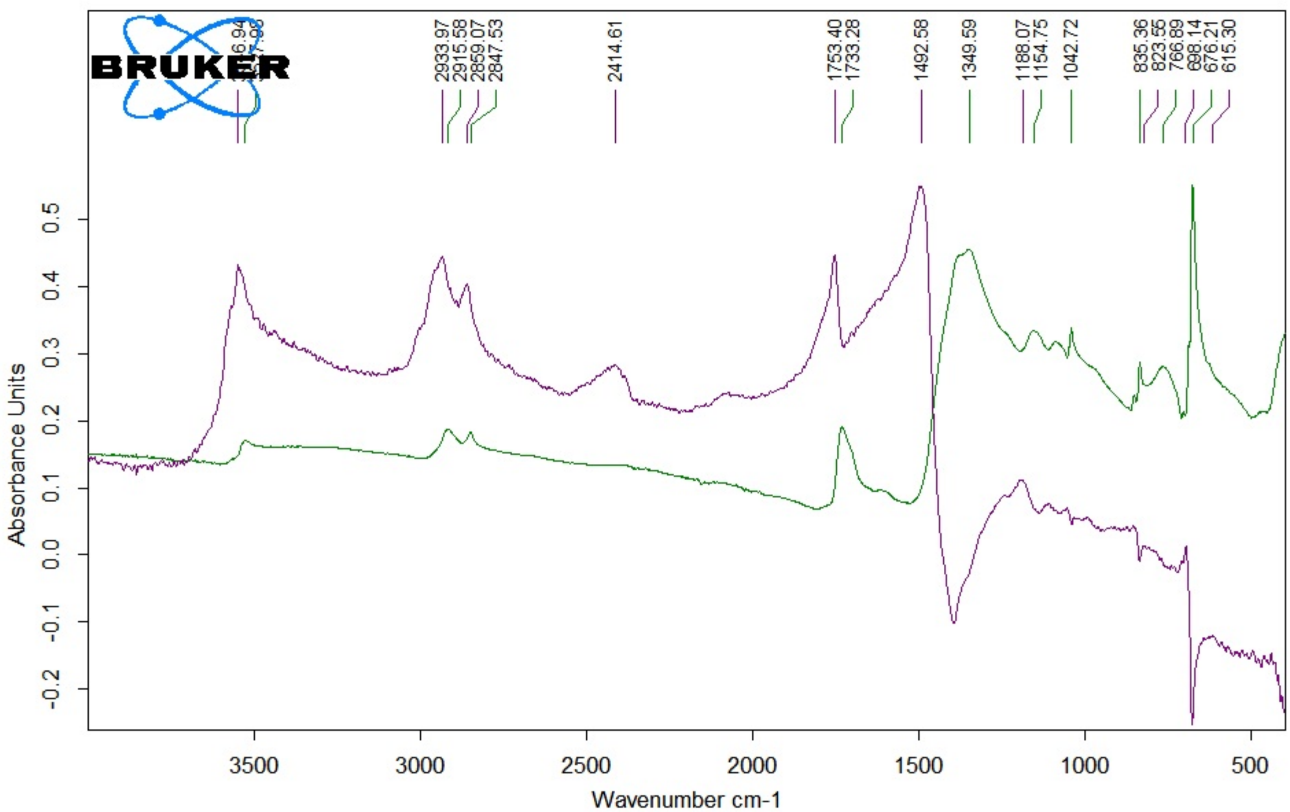
CHEMICAL COMPOUNDS:

$2\ PbCO_3 \cdot Pb(OH)_2$

$C_{15}H_{20}O_6$

$Cu(OH)_2 \cdot (CH_3COO)_2 \cdot 5\ H_2$

C



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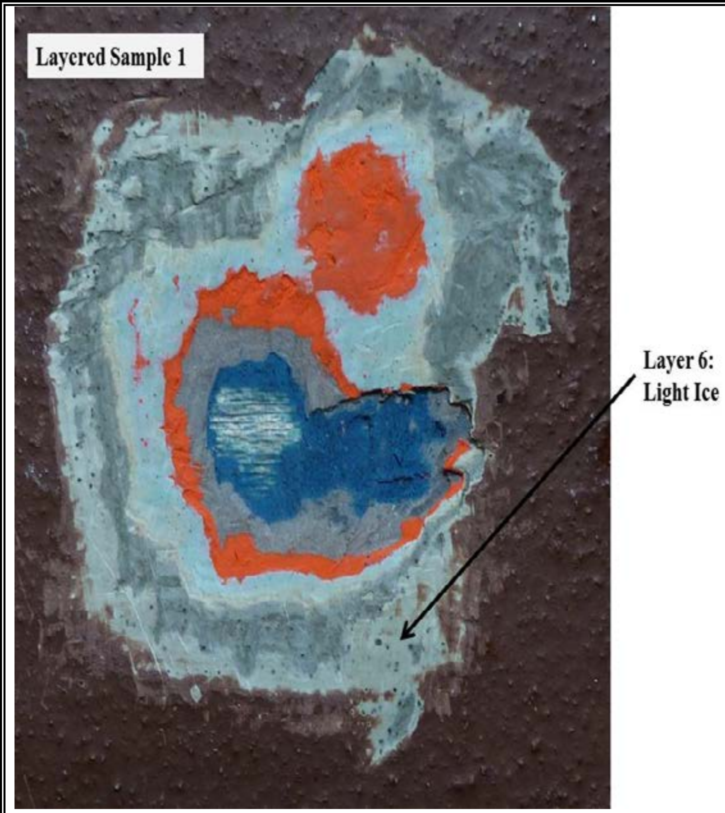
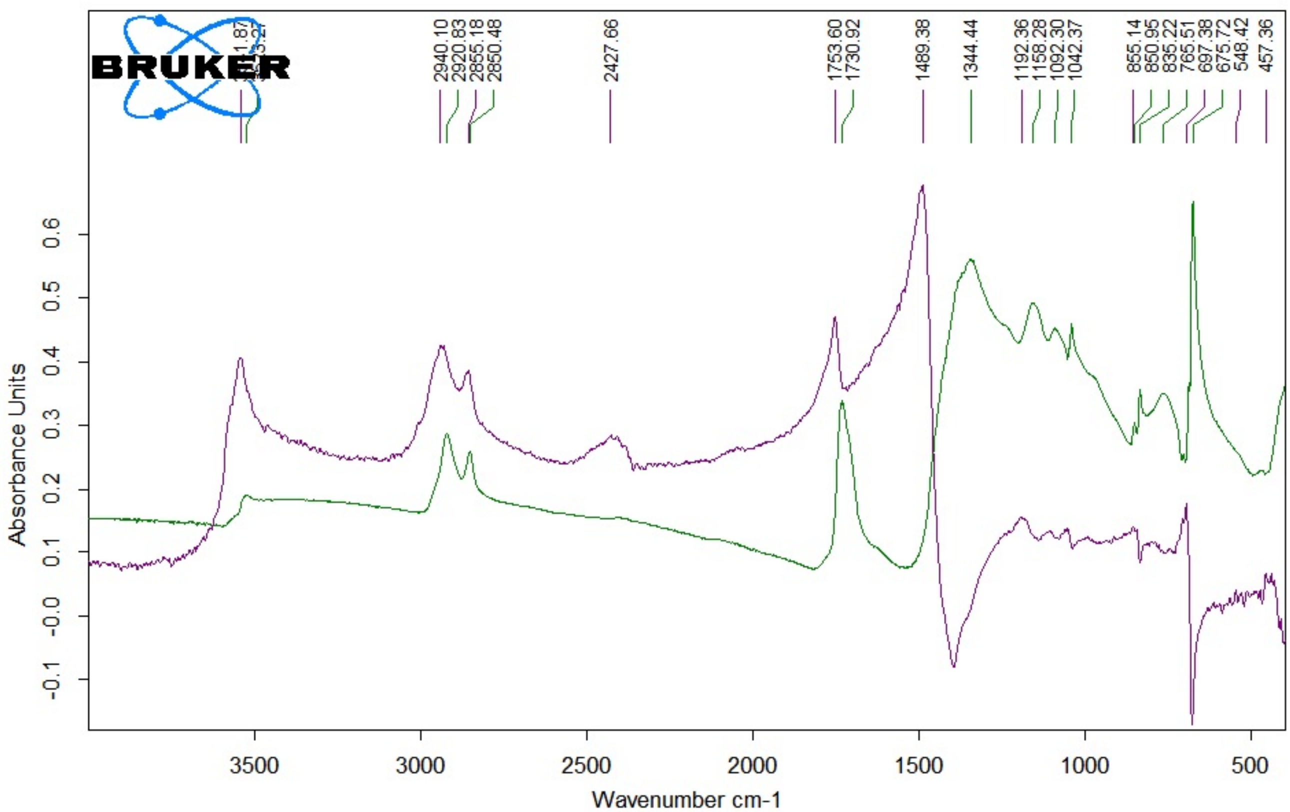


Alpha-P DRIFTS vs. ATR Spectra

All samples are on wood and pigments are in raw linseed oil

Layered Sample 1 Layer 6 vs. Sample 19
PIGMENTS:
small amount of Dark Ice Color (Lead White, Rosin, Verdigris, Lampblack), White Lead
CHEMICAL COMPOUNDS:
$2\ PbCO_3 \cdot Pb(OH)_2$
$C_{15}H_{20}O_6$
$Cu(OH)_2 \cdot (CH_3COO$



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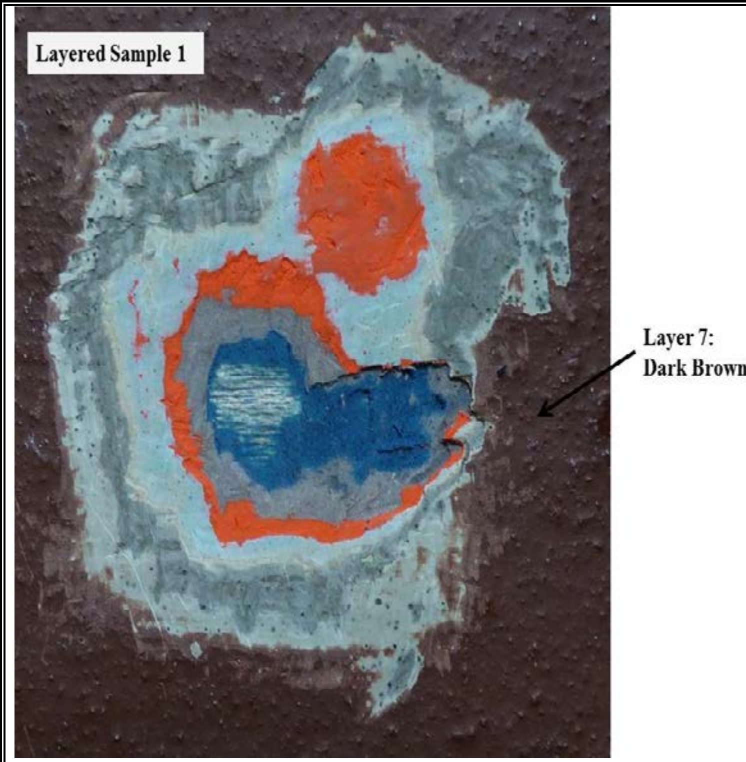


Alpha-P DRIFTS vs. ATR Spectra

All samples are on wood and pigments are in raw linseed oil

Layered Sample 1 Layer 7 vs. Sample 3

PIGMENTS:

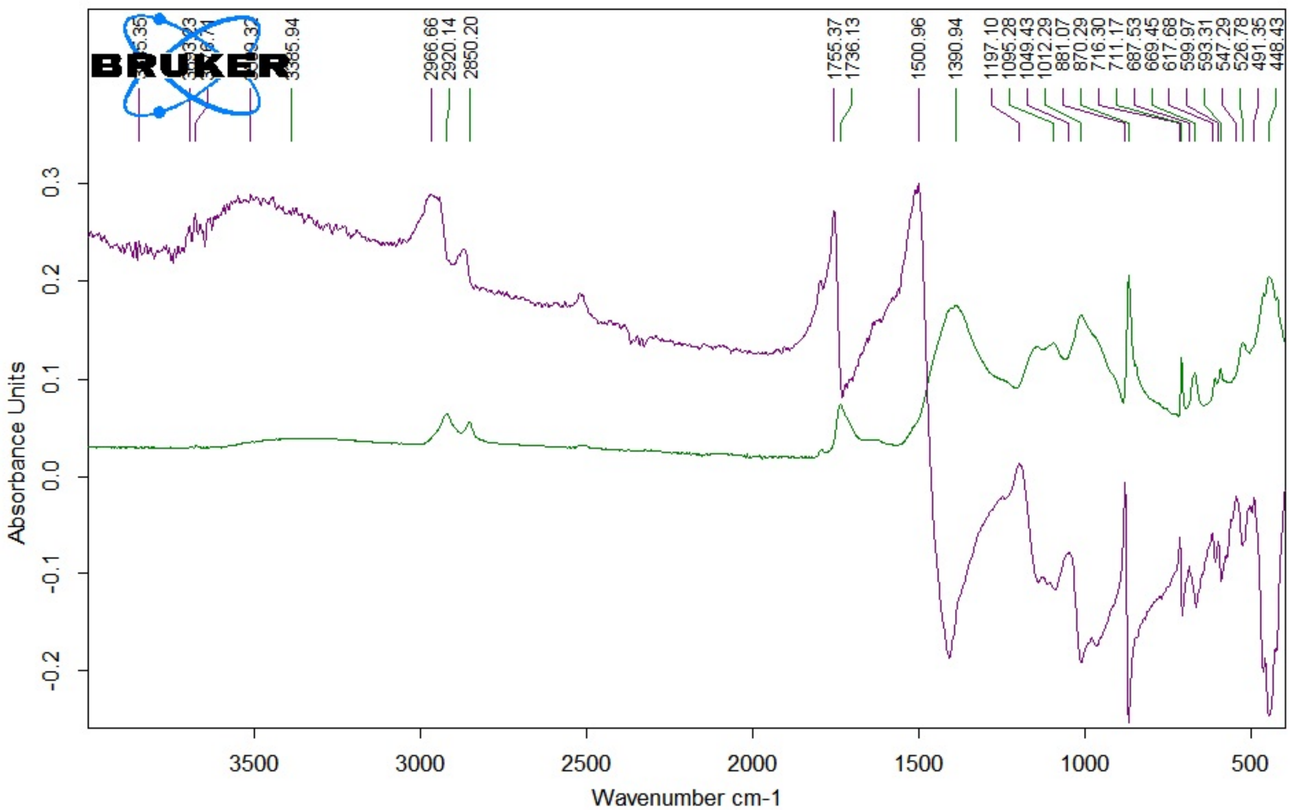
Red Ochre, small amount Red Lead, $CaCO_3$

CHEMICAL COMPOUNDS:

Fe_2O_3

Pb_3O_4

$CaCO_3$



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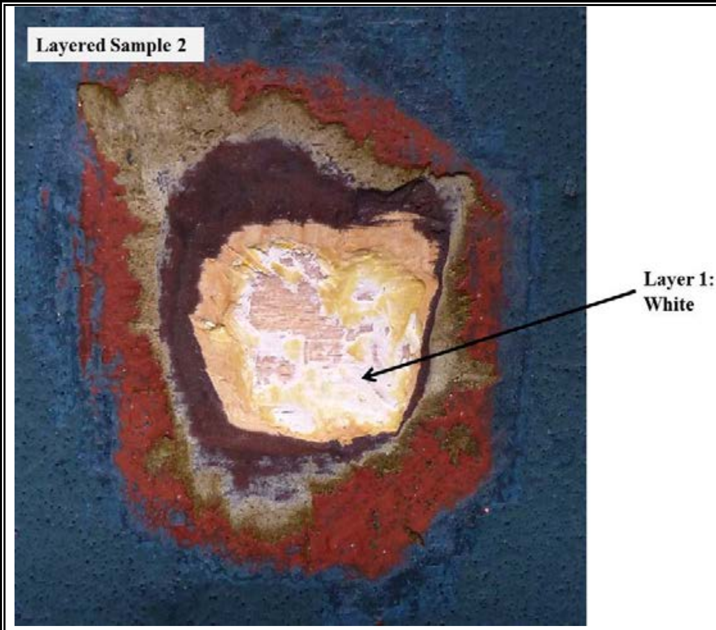


Alpha-P DRIFTS vs. ATR Spectra

All samples are on wood and pigments are in raw linseed oil

Layered Sample 2 Layer 1 vs. Sample 21

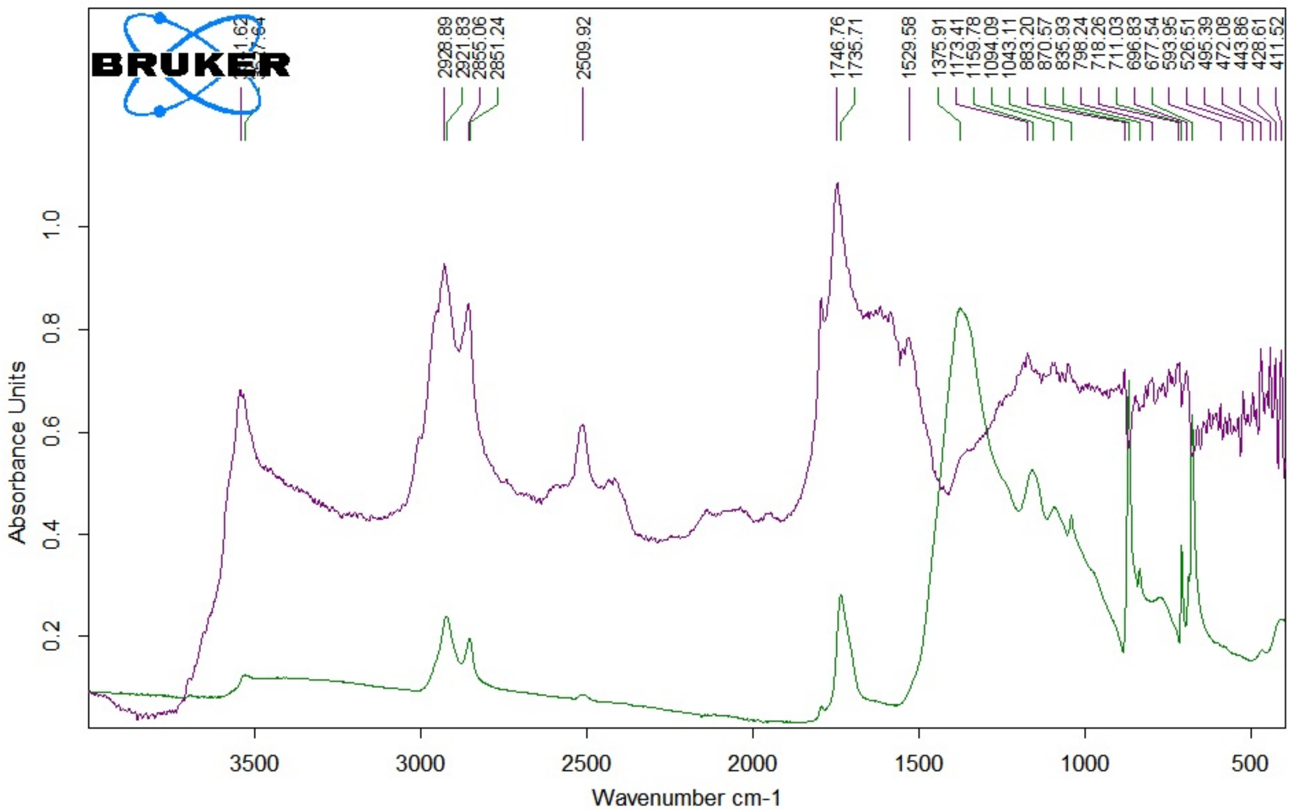
PIGMENTS:

Lead White, $CaCO_3$

CHEMICAL COMPOUNDS:

$CaCO_3$

$2\ PbCO_3 \cdot Pb(OH)_2$



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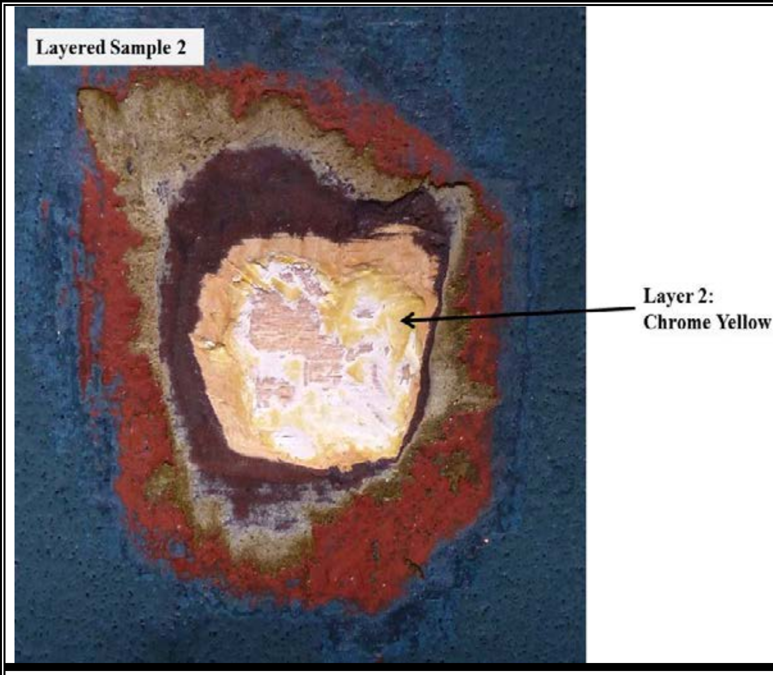


Alpha-P DRIFTS vs. ATR Spectra

All samples are on wood and pigments are in raw linseed oil

Layered Sample 2 Layer 2 vs. Sample 15

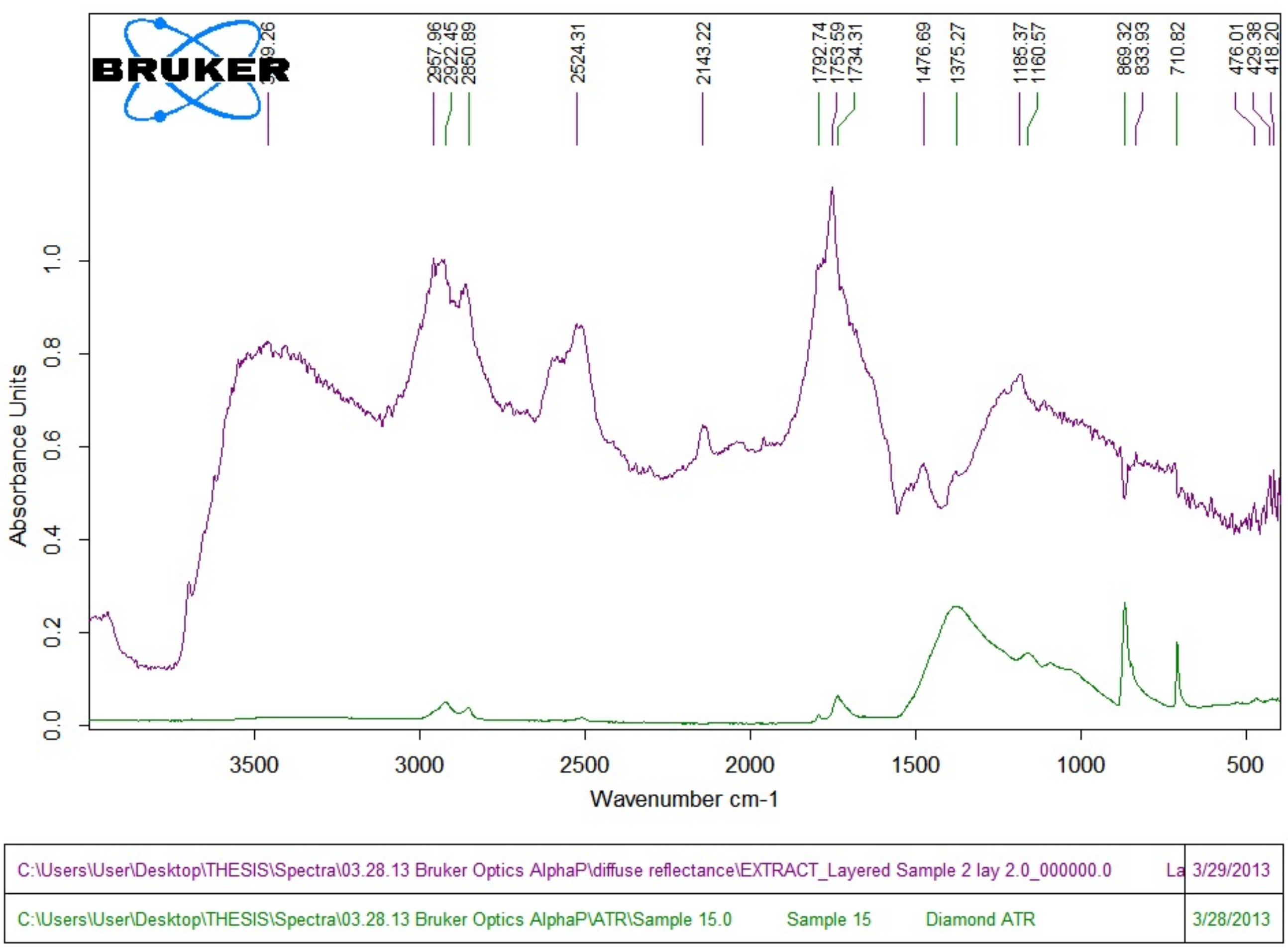
PIGMENTS:

Chrome Yellow Deep, $CaCO_3$

CHEMICAL COMPOUNDS:

$PbCrO_4$

$CaCO_3$



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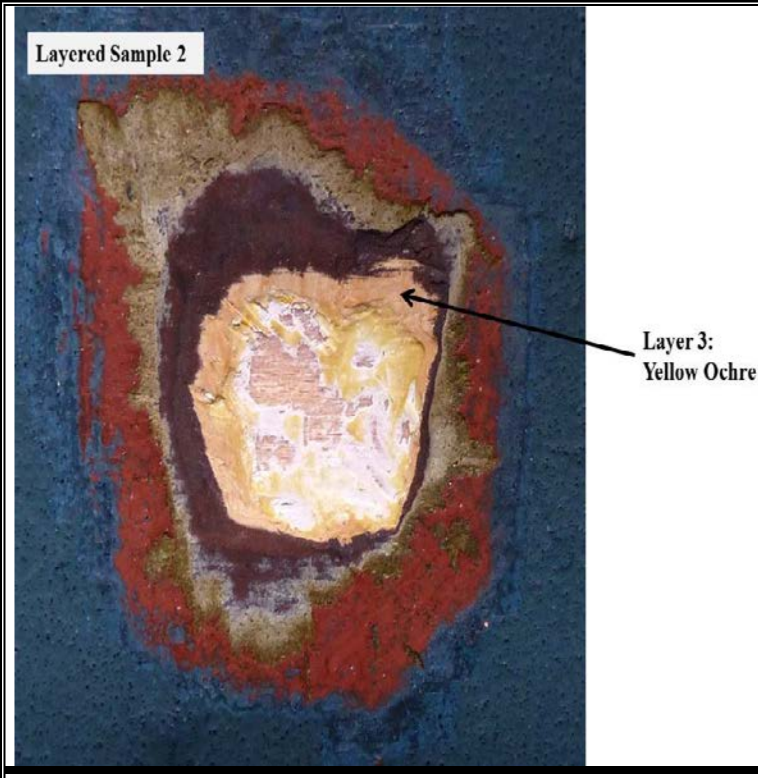


Alpha-P DRIFTS vs. ATR Spectra

All samples are on wood and pigments are in raw linseed oil

Layered Sample 2 Layer 3 vs. Sample 16

PIGMENTS:

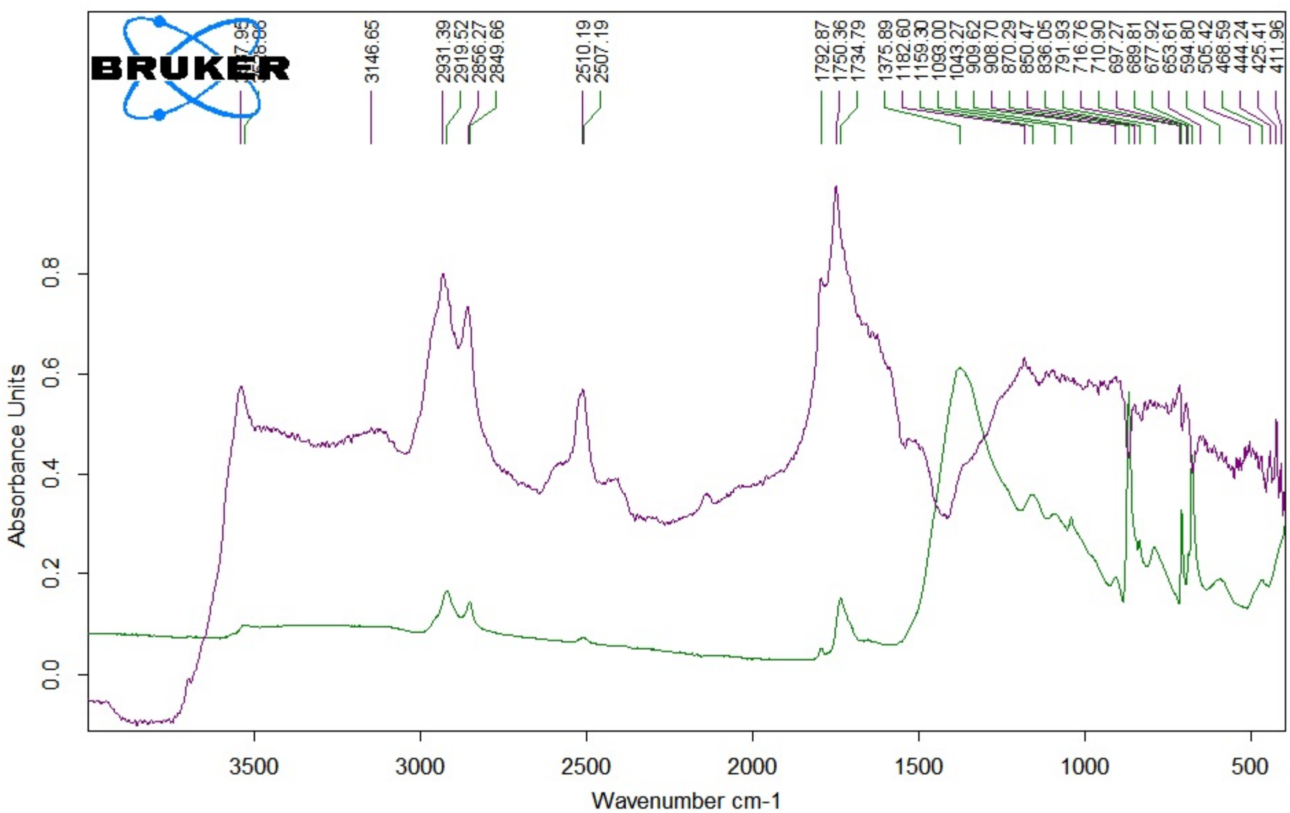
Yellow Ochre, Lead White, $CaCO_3$

CHEMICAL COMPOUNDS:

$2\ PbCO_3 \cdot Pb(OH)_2$

FeO(OH))

$CaCO_3$



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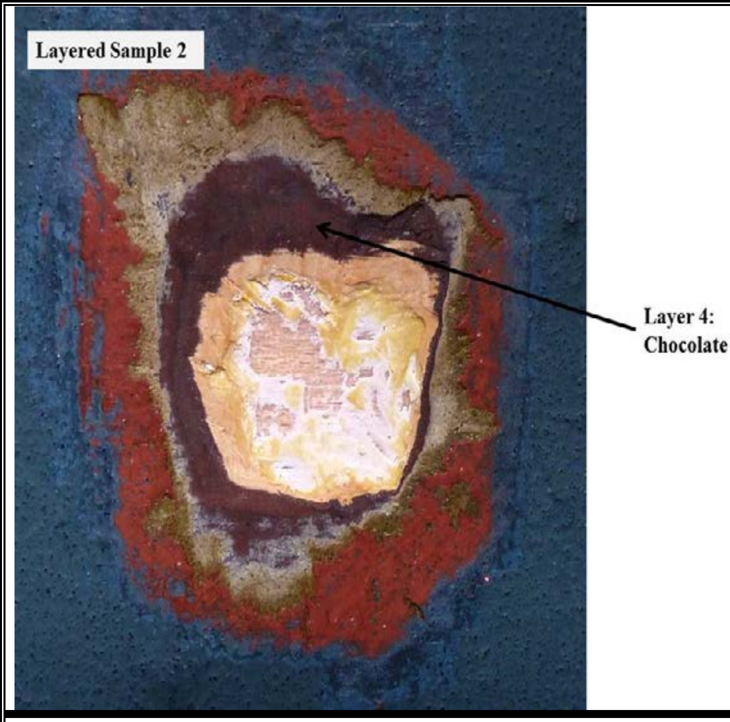


Alpha-P DRIFTS vs. ATR Spectra

All samples are on wood and pigments are in raw linseed oil

Layered Sample 2 Layer 4 vs. Sample 14

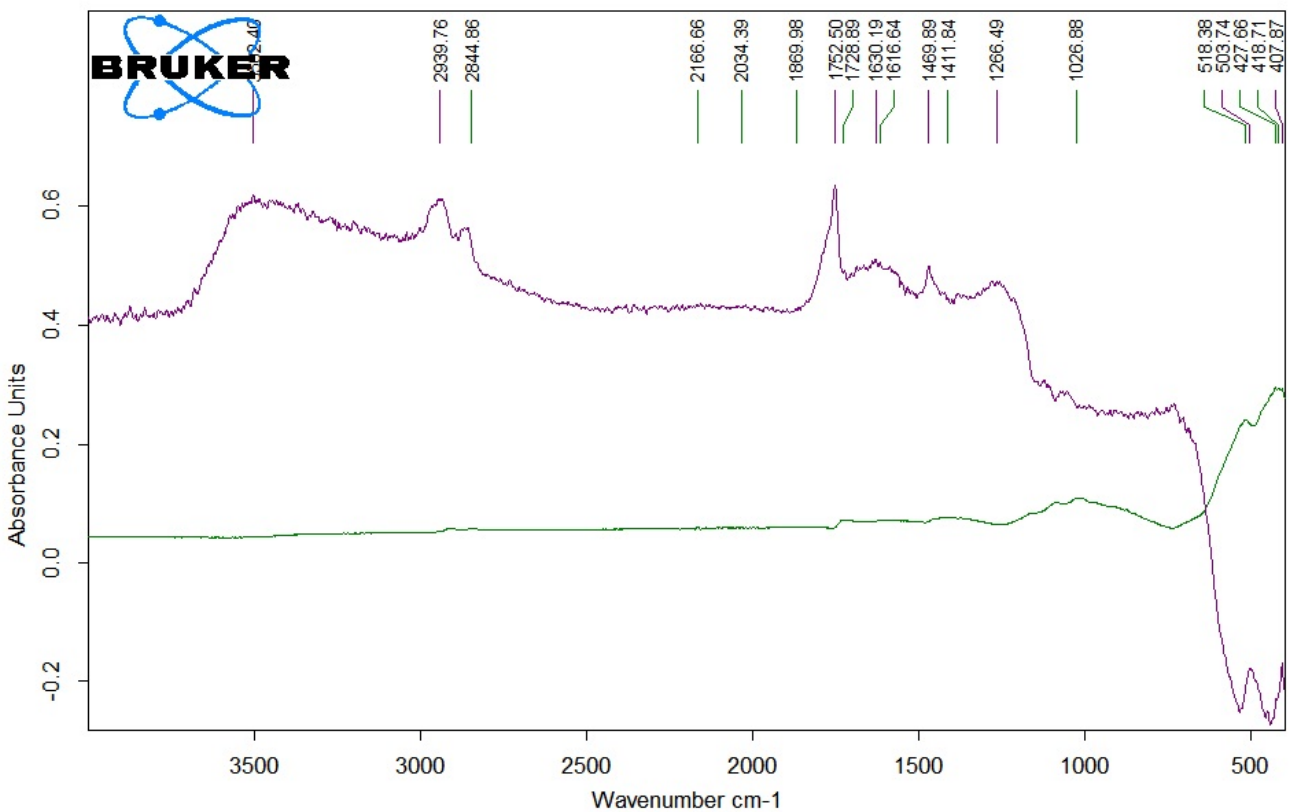
PIGMENTS:

Spanish Brown (Caput Mortuum), Lampblack

CHEMICAL COMPOUNDS:

Fe_2O_3

C



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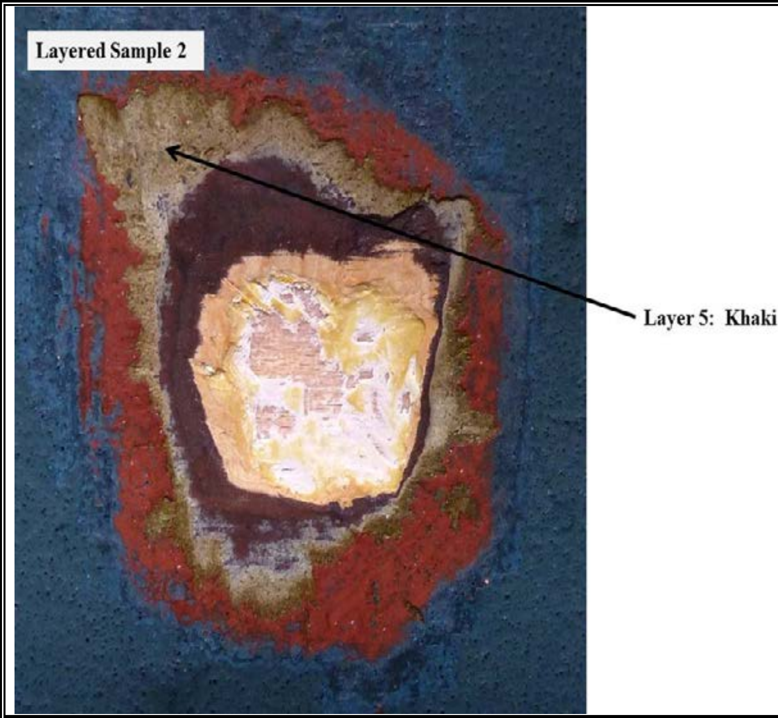


Alpha-P DRIFTS vs. ATR Spectra

All samples are on wood and pigments are in raw linseed oil

Layered Sample 2, Layer 5 vs. Sample 4

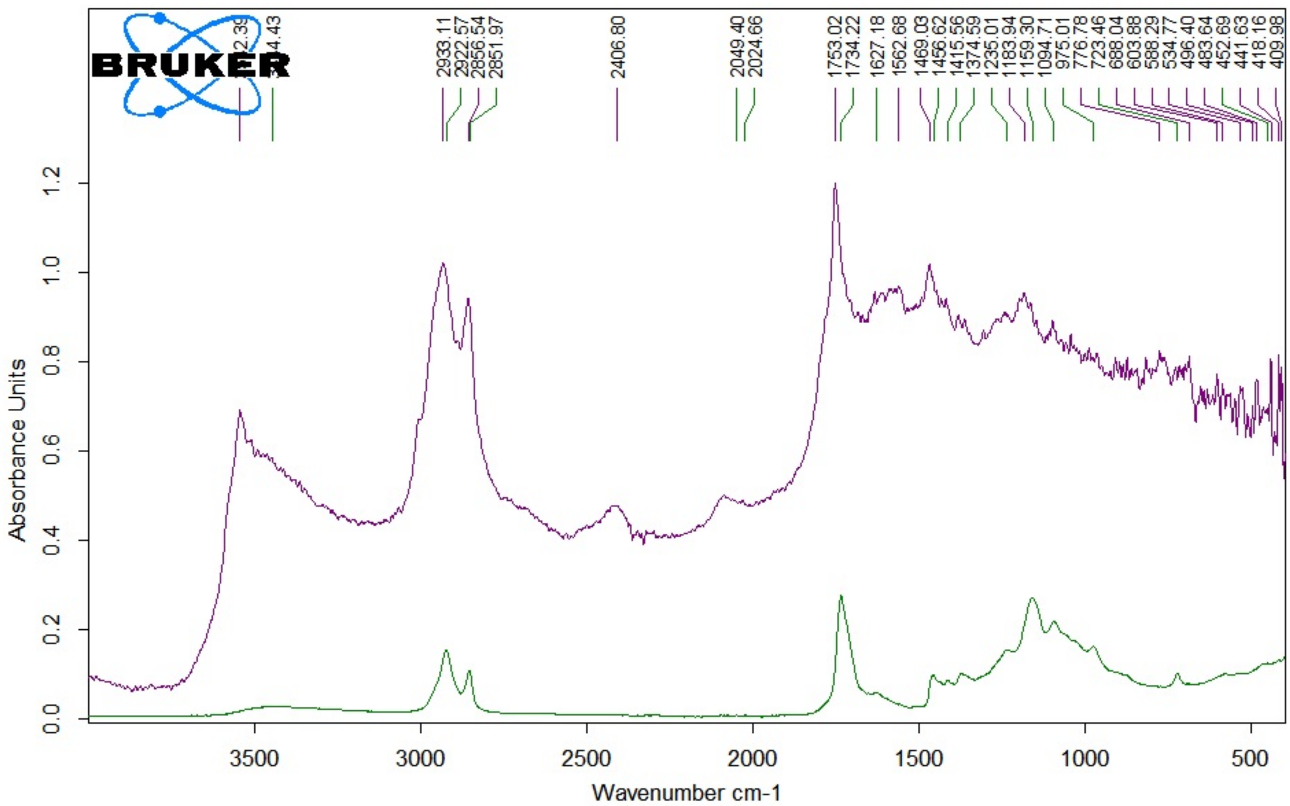
PIGMENTS:

Verdigris, Yellow Ochre, small amount Lead White

CHEMICAL COMPOUNDS:

$Cu(OH)_2 \cdot (CH_3COO)_2 \cdot 5\ H_2O$

$FeO(OH))_;\ 2PbCO_3 \cdot Pb(OH)_2$



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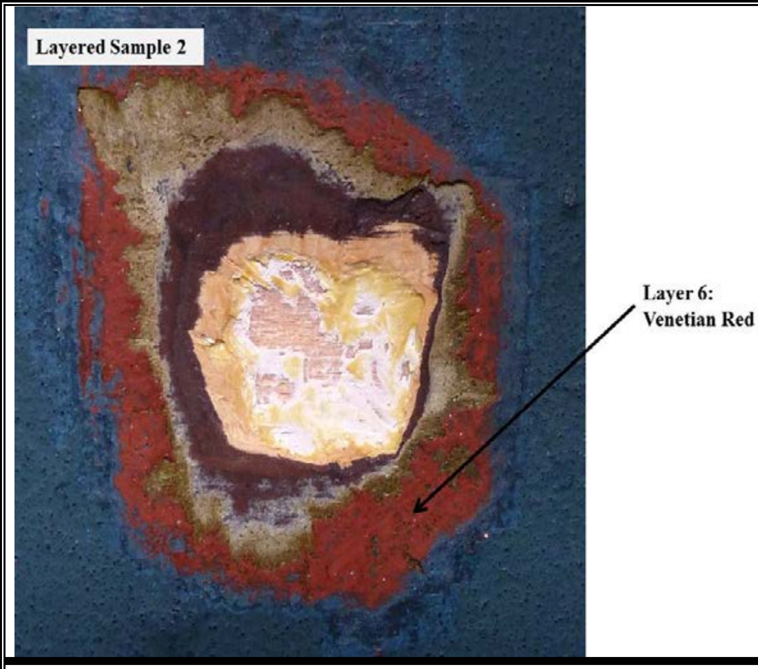


Alpha-P DRIFTS vs. ATR Spectra

All samples are on wood and pigments are in raw linseed oil

Layered Sample 2 Layer 6 vs. Sample 23

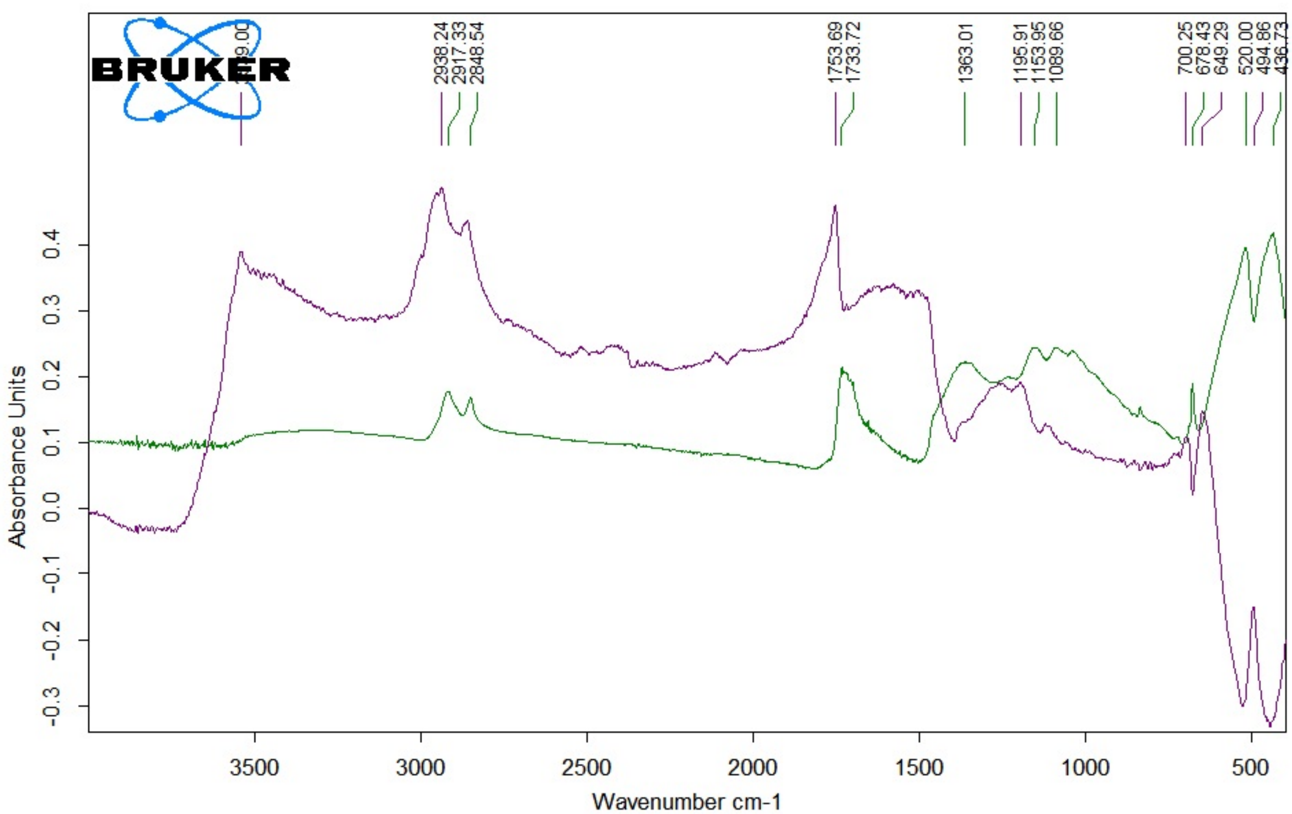
PIGMENTS:

Venetian Lead, Lead White

CHEMICAL COMPOUNDS:

$CaFe_2O_7S$

$2\ PbCO_3 \cdot Pb(OH)_2$



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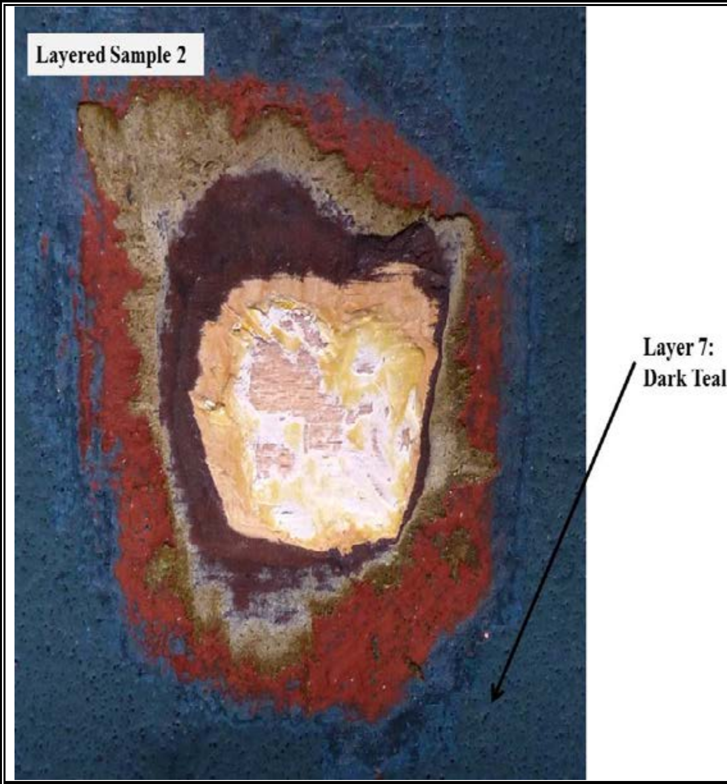


Control Sample Data Sheet

All samples are on wood and pigments are in raw linseed oil

Layered Sample 2 Layer 7 vs. Sample 2

PIGMENTS:

Prussian Blue, Yellow Ochre, Lead White, $CaCO_3$

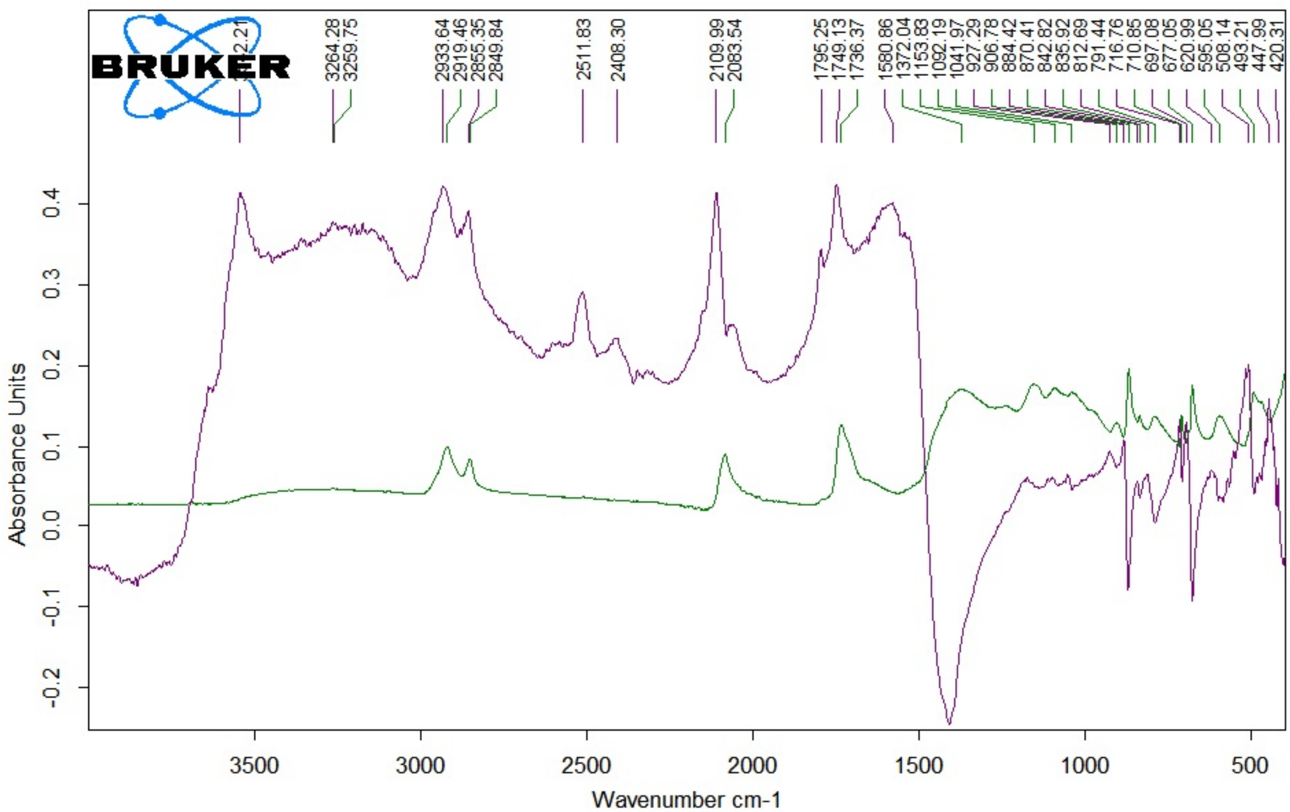
CHEMICAL COMPOUNDS:

$Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$

Fe_2O_3

$2PbCO_3 \cdot Pb(OH)_2$

$CaCO_3$



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